of powdered sodium cyanide and 225 cc. of 95% alcohol was refluxed for ninety hours. All of the chloride and most of the sodium cyanide were initially in solution. After refluxing, the solution was decanted and the insoluble salts washed with alcohol.

The combined alcoholic solutions were returned to the flask along with 8 g. of sodium hydroxide in 25 cc. of water and refluxed for ninety-six hours. The product was evaporated to dryness on the steam-bath, granulated, and dried at 105° to remove the alcohol. The dried soap was dissolved in hot water, acidified with hydrochloric acid and extracted with ether. The ether solution was washed with water and evaporated on the steam-bath. The residue was a light colored oil weighing 29.9 g.

The mixed acids were dissolved in 700 cc. of 95% alcohol and 9 g. of anhydrous lead acetate dissolved by heating. On standing overnight at 25°, 20.1 g. of precipitate was obtained which melted at 83–88°. By cooling to 0° a further crop of 1.0 g. melting at 80–83° was obtained. In the filtrate was dissolved an additional 4 g. of lead acetate. On cooling to 0°, 4.6 g. melting at 60–70° was obtained making a total yield of 25.7 g. of crude salt equivalent to 18.8 g. of elaidic acid or 63% of the mixed acids.

The filtrates containing the oleic acid were combined and concentrated to 190 cc. On cooling to 0°, 0.5 g. of gum precipitated which was probably largely lead oleate and was discarded. The filtrate was evaporated to dryness, taken up in ether, washed with dilute nitric acid and water and the ether evaporated. The residual oil, weighing 10.1 g., was dissolved in 275 cc. of 95% alcohol, 1 g. of lithium hydroxide dissolved by heating, and the solution filtered hot. Four crops of lithium oleate were taken, the first at 25° and the rest at 0° with progressive concentration of the solution. The combined weight was 6.1 g., the first crop melting at 225° and the last at 223°. The calculated amount of liquid acid was obtained from the crystallized lithium oleate by addition of dilute hydrochloric acid, extraction with ether, washing, evaporation of the solvent and drying *in vacuo*.

Anal. Calcd. for $C_{18}H_{34}O_2$: neut. equiv., 282.3; iodine no., 89.9. Found: neut. equiv., 283; iodine no., 89.5.

In order to characterize definitely the acid as oleic, it was converted into the *p*-phenylphenacyl ester.[12] This melted at 57.5–59° after three crystallizations while that from a sample of natural oleic acid purified through the lithium salt melted at 58.5–60° after two crystallizations. The mixed melting point was 58–59.5°.

The first crop of 20.1 g. of lead elaidate on recrystallization from 550 cc. of alcohol and 5 cc. of acetic acid gave 18.5 g. melting at 87–89°. On shaking with dilute nitric acid and ether, and evaporation of the solvent, the calculated amount of solid acid was obtained. After two crystallizations from 95% alcohol at 0°, it melted at 44°.

Anal. Calcd. for $C_{18}H_{34}O_2$: neut. equiv., 282.3; iodine no., 89.9. Found: neut. equiv., 282; iodine no., 89.6.

The mixed melting point with a sample of elaidic acid freshly prepared from natural oleic acid and melting also at 44° showed no depression.

Summary

Oleic and elaidic acids have been synthesized by a procedure which does not permit the formation of structural isomers and which should be of general use for the synthesis of unsaturated fatty acids.

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[12] Drake and Bronitsky, THIS JOURNAL, **52**, 3715 (1930).

STANFORD UNIVERSITY, CALIF.

RECEIVED MARCH 19, 1934

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Tautomerism of the Aminonaphthoquinones

BY LOUIS F. AND MARY FIESER

In continuation of our potentiometric study of the unstable oxido-reduction systems formed by the aminophenols and their primary oxidation products,[1] we have applied similar methods of investigation to a survey of the corresponding compounds in the naphthalene series. It was of particular interest to see if the potentiometric method would furnish any information regarding the possible tautomerism of the aminonaphthoquinones to hydroxynaphthoquinone-imines, and to apply to this problem the general theory regarding such tautomeric equilibria which was developed in an earlier paper.[2]

Nearly all of the possible di- and tri-substituted naphthalenes containing either hydroxyl or amino groups or both in the 1,2-, 1,4- or 1,2,4-positions have been investigated. The oxidants formed in the course of the electrometric titration of these substances represent in many cases quinone-imines or di-imines which are unknown in the solid state and which are quite sensitive to acid or alkaline hydrolysis, but they display for the most part considerable stability in neutral or weakly alkaline buffer solutions, particularly when the reductants used are of a high degree of purity. The oxidants from 2-amino-1-naphthol and 2,3-diamino-1-naphthol, however, proved to be too unstable to per-

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[1] Fieser, THIS JOURNAL, **52**, 4915 (1930).

[2] Fieser, *ibid.*, **50**, 439 (1928).

mit characterization even by the method of discontinuous titration.[1]

Naphthoquinone-imines and Di-imines

Table I summarizes the results of the series of measurements with 1,4-aminonaphthol. The figures in the fourth column indicate the relative stability of the solutions at the point of half-oxidation. Where the velocity of decomposition is given as zero this indicates that no drift in potential was observed in the time required for an ordinary titration (about ten minutes); in the other cases the titrations were discontinuous. The curve relating the potential at half-oxidation (E_n) to P_H was found to include two characteristic slopes, the quantity $-\Delta E_n/\Delta P_H$ having the value of 0.05912 v. in the more acidic region and of 0.02956 v. at the alkaline end. For convenience these are reported in the Table as "0.06" and "0.03" slopes. The former relationship indicates that neither the oxidant nor the reductant is ionized in the neutral and weakly acidic solutions; the decrease in the slope at higher P_H is due to the dissociation of the acidic hydroxyl group of the reductant. The equation given at the top of the table defines the potential of the system in the limited region of P_H investigated. Approximate constants were obtained graphically and adjusted to give a "best" curve.

TABLE I[a]

POTENTIALS OF THE SYSTEM FROM 1,4-NAPHTHOQUINONE-IMINE (25°)

E_0 = 0.5416 v. $K_r^a = 1.78 \times 10^{-10}$

$$E_n = E_0 + E_h + 0.02956 \log [1 + K_r^a/[H^+]]$$

P_H	Hydrogen elec. potential, E_h, v.	Potential when [Ox.] = [Red.], E_n, v.	Velocity constant, $-\Delta E/\Delta t$, mv. per min.	E_n (found − calcd.), mv.	Nature of slope, $-\Delta E_n/\Delta P_H$
6.05	−0.3587	0.1835	11.8	0.6	0.06
6.67	.3944	.1477	5.1	.5	
7.02	.4149	.1263	3.9	−0.4	
8.07	.4769	.0640	0	−0.7	
8.58	.5079	.0328	0	−1.7	
8.88	.5250	.0168	0	−1.4	
9.26	.5479	− .0050	0	−2.3	
9.87	.5839	.0298	1.7	1.4	
10.67	.6313	.0615	2.0	−0.7	0.03
11.49	.6795	.0867	2.7	−0.3	
11.86	.7007	.0980	3.0	−1.0	
12.71	.7525	.1216	8.1	1.3	

[a] The potentials are referred to the hydrogen electrode standard. The term E_0 is here defined (contrary to the convention of certain other authors) as the normal potential referred to the *undissociated components* of the system; K_r^a is the acidic dissociation constant of the reductant.

Results for various other oxido-reduction systems are listed in Table II and the results will be discussed in later sections. Since the normal potential of the β-naphthoquinone system in aqueous solution was desired for comparison, and since the only earlier determination in this medium[3] is

TABLE II

POTENTIALS AT 25°

Measurements in limited P_H regions, where $E_n = E_0 + E_h$

Reductant	P_H	Potential when [Ox.] = [Red.], E_n, v.	Velocity constant, $-\Delta E/\Delta t$, mv. per min.	Normal potential E_0, v.
1,2-Aminonaphthol E_0 = 0.616 (av.)	6.67	0.220	20	0.614
	7.02	.199	15	.614
	7.58	.166	11	.614
	8.04	.142	9	.617
	8.07	.142	8	.619
	8.07	.140	9	.618
	8.58	.111	10	.619
	8.58	.110	10	.618
	8.88	.090	13	.615
1,2-Aminonaphthol-4-sulfonic acid E_0 = 0.691 v. (av.)	6.67	0.296	16	0.690
	7.02	.275	14	.690
	7.58	.245	13	.693
	8.07	.213	14	.690
	8.58	.185	14	.693
1,4-Naphthalenediamine E_0 = 0.6435 v. (av.)	8.07	0.1668	3.0	0.6439
	8.58	.1354	0.8	.6433
	8.88	.1197	.7	.6447
	9.26	.0959	.4	.6438
	9.87	.0572	.3	.6441
	10.68	.0108	.4	.6421
	11.49	.0372	.2	.6428
1,2,4-Triaminonaphthalene E_0 = 0.391 v. (av.)	7.02	−0.022	2.7	0.392
	7.60	.059	0	.390
	7.60	.060	0	.389
	7.69	.064	0	.391
	7.87	.074	0	.391
	8.02	.085	0	.389
	8.02	.085	0	.389
	8.57	.115	0	.391
	8.90	.133	0	.393
	8.90	.133	0	.394
β-Naphthohydroquinone E_0 = 0.5549 v. (av.)	6.05	0.1962	0	0.5549
	6.05	.1958	0	.5545
	6.67	.1606	0	.5550
	6.67	.1602	0	.5546
	7.02	.1406	0	.5555
	7.02	.1400	0	.5549
3,4-Diamino-1-naphthol E_0 = 0.3817 (av.)	5.45	0.0548	4.4	(0.3767)
	7.02	− .0325	0	.3824
	7.57	.0655	0	.3824
	7.60	.0681	0	.3811
	8.04	.0949	0	.3806
	8.07	.0941	0	.3828
	8.58	.1277	0	.3802
	8.88	.1427	0	.3823
	9.26	.1639	0	(.3963)

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(3) Conant and Fieser, THIS JOURNAL, **46**, 1858 (1924).

open to question,[4] a redetermination with the improved technique is included in the table. The value of 0.483 v. for α-naphthoquinone at 25° in 50% alcoholic solution given by Conant and Fieser[3] was checked by three closely agreeing titrations of the hydroquinone with potassium ferricyanide in 50% alcohol, 0.1 *N* in hydrochloric acid and 0.2 *N* in lithium chloride (av., 0.4839 v.).

Hydroxynapthoquinone has been studied in alcoholic solution,[3,4] but for the present purposes information regarding the value in aqueous solution, and the acidic strength of the compound, was desired. A complete characterization of the system, together with the electrode potential equation, is given in Table III. The E_n:P_H curve revealed one acidic dissociation constant for the oxidant (K_0) and two for the reductant (K_{r_1}, K_{r_2}). The marked resemblance of hydroxynaphthoquinone to the carboxylic acids has been recognized from chemical evidence;[5] it is now apparent that the substance is an even stronger acid than acetic acid.

TABLE III

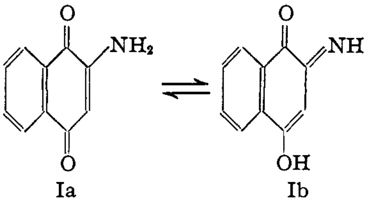
POTENTIALS OF THE SYSTEM FROM 2-HYDROXY-1,4-NAPHTHOQUINONE (25°)

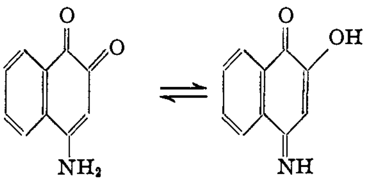
$E_0 = 0.3511$ v. $K_0 = 1.05 \times 10^{-4}$. $K_{r_1} = 2.09 \times 10^{-9}$ $K_{r_2} = 1.95 \times 10^{-11}$. $E_n = E_0 + E_h + 0.02956 \log [1 + K_{r_1}/[H^+] + K_{r_1}, K_{r_2}/[H^+]^2] - 0.02956 \log [1 + K_0/[H^+]]$.

P_H	Hydrogen elec. potential, E_h, v.	Potential when [Ox.] = [Red.], E_n, v.	E_n (found − calcd.), mv.	Nature of slope, $-\Delta E_n/\Delta P_H$
0.33	−0.0194	0.3300	−1.7	0.06
1.03	.0611	.2901	0.1	
1.75	.1037	.2483	.9	
2.58	.1523	.1994	−1.1	
3.29	.1945	.1529	−1.3	
3.82	.2259	.1193	0.9	
4.28	.2531	.0799	−4.0	
4.91	.2901	.0334	1.4	0.09
5.61	.3314	− .0287	0.1	
7.02	.4149	.1531	.6	
8.30	.4908	.2631	−0.2	
9.06	.5354	.3165	2.1	
9.78	.5780	.3637	0	(0.06)
10.35	.6117	.3962	−1.4	
11.49	.6795	.4444	−1.9	0.03
12.03	.7115	.4589	1.2	
12.64	.7470	.4774	0.7	
12.92	.7642	.4849	2.0	

The Aminonaphthoquinones

Although the aminonaphthoquinones Ia and IIa have been known for a number of years, little evidence has accumulated to show whether the substances exist in the forms indicated or in the tautomeric forms Ib and IIb. The first isomer has been regarded as having the aminoquinone structure, since it displays acidic properties only in alcoholic solution. Most authors appear to have followed Kehrmann[6] in representing the second of these compounds as hydroxynaphthoquinone-imine, IIb, for the reason that the substance dissolves in alkali. It is curious, however, that although it must have been apparent to everyone who has prepared the compound that the quinone dissolves only in a strongly alkaline medium and not in dilute ammonia or soda solution, no comment has been made on this divergence from the behavior to be expected of a substance related as closely as is IIb to the strongly acidic hydroxynaphthoquinone. The fact is that the deportment of the quinone in alkali reveals nothing of the structure of the substance in other media. A further argument in favor of formula IIb based upon oximation experiments has been advanced in a recent paper by Goldstein, Koetschet and Duboux.[7] While the argument possesses the weight of such circumstantial evidence as is available, it appears to us to lack conviction. In a system as mobile as the one under discussion is likely to be, one tautomer may well enter much more rapidly into reaction than the other and thus determine the outcome of the transformation.


Ia Ib


IIa IIb

The potentiometric method would appear to offer a particularly valuable means of studying this type of tautomerism for it is concerned with equilibria and not with reaction rates. It soon will be evident, moreover, that it is not necessary to reason from analogy, as in the study of the tautomerism of the hydroxyquinones,[2] for the

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[4] Fieser and Peters, THIS JOURNAL, **53**, 793 (1931).

[5] Fieser, *ibid.*, **48**, 2922 (1926).

[6] Kehrmann and Täuber, *Ber.*, **27**, 3337 (1894).

[7] Goldstein, Koetschet and Duboux, *Helv. Chim. Acta*, **16**, 241 (1933).

direct potentiometric characterization of the compounds in question is sufficient to reveal their true natures.

Dilute solutions (0.0014 *M*) of the aminoquinones are quite stable at 25° over the entire *P*H range and no difficulty was experienced in making the measurements. The variation of the potential at half-oxidation with hydrogen-ion concentration is given in Fig. 1. Considering first the simpler Curve B for the amino-α-naphthoquinone, it will be observed that in the range *P*H 4.9–8.6 the points fall on a straight line having the 0.06 slope characteristic of the hydrogen electrode. Here obviously neither the oxidant nor the reductant is ionized and $E_0 = E_n - E_h$. On passing to more acidic solutions there is an upward inflection to the 0.09 slope; this must be due to the removal of a portion of the reductant from the oxido-reduction equilibrium as the result of a basic ionization of this component. The intersection of the two curves gives pK^b_r, which refers to the basic dissociation of 2-amino-1,4-dihydroxynaphthalene. This and all other basic dissociation constants reported in the present paper are defined by the equation $K^b = [\text{Amine}][H^+]/[\text{Amine-ion}^+]$.[8]

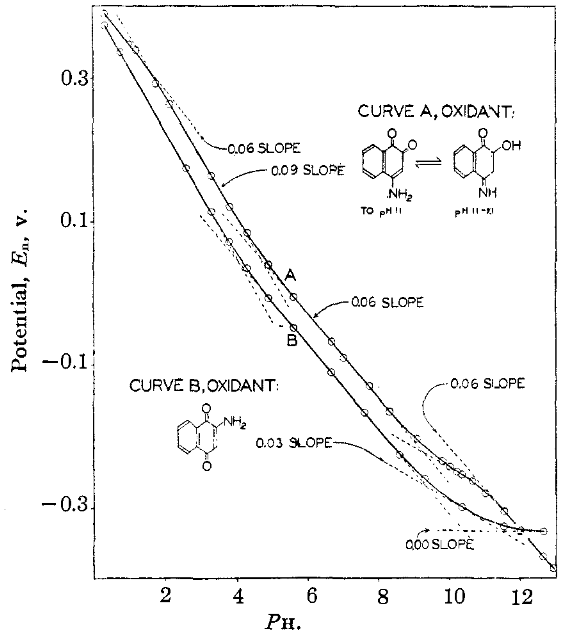

Fig. 1.—Relationship between *P*H and the potential of half-oxidation for the aminonaphthoquinones.

On going from the neutral to the alkaline range the curve passes through a potential 0.03 slope to a zero slope, which indicates the progressive withdrawal of the active reductant through a first and then a second acidic ionization. Reduction of the quinone in a strongly alkaline solution yields the reductant in the form of the bivalent anion and the potential becomes independent of the hydrogen-ion concentration. The acidic constants, $K^a_{r_1}$ and $K^a_{r_2}$, may be obtained from the intersections of the straight lines.

It is evident that the E_n:*P*H curve reveals three ionization constants all referring to the reductant; an ionization of the oxidant would tend to lower the potential rather than raise it and hence give an inflection in the opposite direction to those noted. These facts are consistent only with formula Ia for the oxidant in question. It is not surprising that 2-amino-1,4-naphthoquinone should be too weakly basic to ionize at *P*H 0.33. Table IV includes, together with a summary of the results, the values found for the various dissociation constants and the electrode equation.

TABLE IV

POTENTIALS OF THE SYSTEM FROM 2-AMINO-1,4-NAPHTHOQUINONE (25°)

E_0 = 0.2827 v. $K^b_r = 9.12 \times 10^{-5}$. $K^a_{r_1} = 2.70 \times 10^{-10}$. $K^a_{r_2} = 5.37 \times 10^{-12}$. $E_n = E_0 + E_h + 0.02956 \log [1 + [H^+]/K^b_r + K^a_{r_1}/[H^+] + K^a_{r_1}, K^a_{r_2}/[H^+]^2]$.

*P*H	Hydrogen elec. potential, E_h, v.	Potential when [Ox.] = [Red.], E_n, v.	E_n (found − calcd.), mv.	Nature of slope, $-\Delta E_n/\Delta P_H$
0.33	−0.0194	0.3733	0.2	0.09
.76	.0447	.3364	−2.4	
2.58	.1523	.1740	−0.6	
3.29	.1945	.1143	1.9	
3.82	.2259	.0718	2.5	
4.28	.2531	.0349	−0.5	
4.91	.2901	− .0069	−1.1	0.06
5.61	.3314	.0489	−0.5	
6.67	.3944	.1124	− .7	
7.60	.4491	.1669	− .6	
8.59	.5079	.2250	− .3	
9.27	.5479	.2602	− .8	
10.35	.6117	.2999	2.8	(0.03)
11.49	.6795	.3251	2.7	
12.03	.7115	.3327	−1.2	0.00
12.64	.7470	.3322	0.4	

The more interesting case is that of the isomeric substance, which may be either an amino-β-naphthoquinone (IIa) or a hydroxy-α-naphthoquinone-imine (IIb), and the relationship between potential and *P*H for this substance is given in Curve A of Fig. 1. In the region *P*H 2.6 to about 10.5 this curve is parallel to B and shows the same characteristic slopes: 0.09, 0.06 and 0.03. In the strongly acidic region, however, Curve A differs from that for the isomer. There is a downward

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[8] This is much more convenient than the expression: $K^b = 1.26 \times 10^{-14}$ [Amine-ion$^+$]/[Amine][H$^+$], used in the earlier paper.[1]

inflection to an 0.06 slope which can only be the result of a decrease in the ratio [Ox.]/[Red.] due to a basic ionization of the oxidant. Calculation shows that the dissociation constant K_0^β of 4-amino-1,2-naphthoquinone is 2.69×10^{-2}. The substance is weakly but definitely basic. That both aminonaphthoquinones are considerably less basic than aniline or the naphthylamines is easily understandable, for they are to be regarded as acid amides rather than as aromatic amines; that the β-quinone derivative is the more basic of the two is probably because of the greater removal of the amino group from the unsaturated carbonyl groups in the molecule.

It is evident that the equation given above (Table IV) for the amino-α-naphthoquinone system needs to be modified only by the inclusion of a term involving the basic dissociation constant of the oxidant in order to be applicable to the isomeric β-naphthoquinone derivative up to about P_H 10.5. This modified equation is to be found at the top of Table V, together with the various constants found. The ionization constants of the reductant do not differ greatly from those for the isomer.

TABLE V

SYSTEM FROM 1,2-DIHYDROXY-4-AMINONAPHTHALENE (25°)

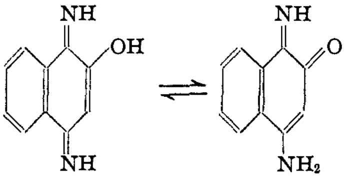
Constants of the reductant: $K_\mathrm{r}^\mathrm{b} = 3.89 \times 10^{-5}$. $K_\mathrm{r}^\mathrm{a} = 4.79 \times 10^{-10}$. β-Oxidant, 4-amino-1,2-naphthoquinone (P_H 0 – 11): $E_0^\beta = 0.3255$ v. $K_\beta^\mathrm{b} = 2.69 \times 10^{-2}$. $E_\mathrm{n} = E_0^\beta + E_\mathrm{h} + 0.02956 \log [1 + [\mathrm{H}^+]/K_\mathrm{r}^\mathrm{b} + K_\mathrm{r}^\mathrm{a}/[\mathrm{H}^+]] - 0.02956 \log [1 + [\mathrm{H}^+]/K_\beta^\mathrm{b}]$.

P_H	Hydrogen elec. potential, E_h, v.	Potential when [Ox.] = [Red.], E_n, v.	E_n (found – calcd.), mv.	Nature of slope, $-\Delta E_\mathrm{n}/\Delta P_\mathrm{H}$
0.33	−0.0194	0.3903	1.0	0.06
1.03	.0611	.3469	1.7	
1.19	.0701	.3394	2.7	
1.75	.1037	.2955	0	
2.14	.1263	.2643	1.0	
2.58	.1523	.2254	−0.9	0.09
3.29	.1945	.1642	− .7	
3.82	.2259	.1209	.9	
4.28	.2531	.0841	.7	
4.91	.2901	.0395	.6	
5.61	.3314	− .0057	−0.6	0.06
6.67	.3944	.0691	− .3	
7.02	.4149	.0913	−1.7	
7.73	.4569	.1299	1.2	
8.30	.4908	.1651	−1.0	
9.06	.5354	.2038	0.5	
9.78	.5780	.2351		
9.98	.5899	.2431	−0.7	0.03
10.21	.6035	.2499	.2	
10.35	.6117	.2543	.3	
10.64	.6291	.2629	...	
10.95	.6486	.2793	...	
11.49	.6795	.3052	...	
12.03	.7115	.3339	−0.5	0.06
12.64	.7470	.3686	.3	
12.92	.7642	.3859	.2	

While the experimental results correspond well with the equation given in the range indicated, there is a marked divergence in the strongly alkaline region. It will be observed in Fig. 1 that Curve A bends sharply downward at about P_H 11 onto the 0.06 slope, a behavior definitely contrary to the requirements of the equation. The nature and the direction of the inflection are such as to indicate an acidic ionization of the oxidant and, since amino-β-naphthoquinone is incapable of such an ionization, it may be inferred that in this region the oxidant has some other structure, presumably that of the tautomer, 2-hydroxy-1,4-naphthoquinone-4-imine. This substance certainly would have an appreciable acidic dissociation constant, K_α^a; it might also have a basic constant, K_α^b, but this assumption is not essential to the following argument. The equation for the tautomer in question is a modification of that given in Table V, for the tautomers have a common reductant and the third term in the equation is thus the same in each case. The normal potential of the β-quinone, E_0^β, is replaced by that for the α-tautomer, E_0^α, and the last term in the equation becomes: $-0.02956 \log [1 + K_\alpha^\mathrm{a}/[\mathrm{H}^+] + [\mathrm{H}^+]/K_\alpha^\mathrm{b}]$. There is no way of judging the magnitude of the three constants concerned, but fortunately it is not necessary to do so in order to determine the character of the E_n:P_H curve in the alkaline region. There can be no doubt that at P_H 11 the basic group of the α-oxidant will be un-ionized, and that the acidic group will be completely ionized. The above term then reduces to: $-0.02956 \log K_\alpha^\mathrm{a}/[\mathrm{H}^+]$. Since the term referring to the ionization of the reductant reduces to $0.02956 \log K_\mathrm{r}^\mathrm{a}/[\mathrm{H}^+]$ above P_H 11, the hydrogen-ion concentrations in the two expressions cancel and the variation of potential with P_H is determined solely by the potential of the hydrogen electrode (E_h) and hence the 0.06 slope is to be expected. This is what is actually found at the alkaline end of the curve, and it is thus evident that the experimental results agree well with the supposition that at about P_H 11 2-hydroxy-1,4-naphthoquinone-4-imine becomes the predominant tautomer. A careful analysis of the curve shows that between P_H 10.4 and 11.5 the solutions contain equilibrium mixtures in which both tautomers are present in appreciable amounts; the β-form is the more stable tautomer on the more acidic side, the change to the α-tautomer is complete at PH 11.5.

It would be of considerable interest to know the normal potential and the ionization constants of the alkali-stable tautomer but no direct determination appears possible. An attempt was made to characterize the isomeric substance produced on the oxidation of 3-hydroxy-4-amino-1-naphthol, for this would be a hydroxyquinone-imine and should conform to the equation discussed above regardless of whether it has the *para* or the *ortho* quinone-imine structure. The oxidant, however, was too unstable to permit an extended study.

The Aminonaphthoquinone-imines and Diimines.—The primary oxidation products of 1,4-diamino-2-naphthol and of 3,4-diamino-1-naphthol are so unstable in acid solution that the study of the tautomerism of these oxidants was necessarily limited to a narrow region of PH, but it nevertheless is possible to draw certain conclusions from the results obtained. In the case of the first reductant oxidation may yield either the hydroxyquinonedi-imine IIIa or the amino-quinone-imine IIIb. At PH 8–9 the first tautomer surely would be present as an anion, the reductant would be un-ionized, and the E_n:PH curve would have a slope of -0.09 v. per PH. At about PH 10–12 the acidic dissociation of the reductant might cause an inflection to an 0.06 slope. The character of the curve for tautomer IIIb would be different, owing to the fact that this oxidant is incapable of acidic ionization. The slope would be 0.06 in the weakly alkaline range and 0.03 in the more strongly alkaline regions. The actual results given in Table VI conform to the latter of these two possibilities, and the substance in question thus clearly exists in the form of 4-amino-1,2-naphthoquinone-1-imine (IIIb) in the solutions studied.



IIIa IIIb

TABLE VI

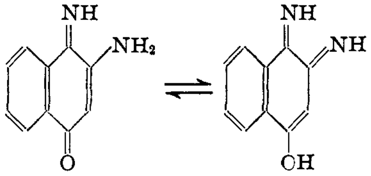
POTENTIALS OF THE SYSTEM: 1,4-DIAMINO-2-NAPHTHOL–4-AMINO-1,2-NAPHTHOQUINONE-1-IMINE (25°)

$E_0 = 0.391$ v. $K_r^a = 3.65 \times 10^{-10}$

$E_n = E_0 + E_h + 0.02956 \log [1 + K_r^a/[H^+]]$

PH	Hydrogen elect. potential, E_h, v.	Potential when [Ox.] = [Red.], E_n, v.	Velocity constant, $-\Delta E/\Delta t$, mv. per min.	E_n (found − calcd.), mv.	Nature of slope, $-\Delta E_n/\Delta$PH
8.04	−0.4755	−0.0847	0	−0.2	0.06
8.07	.4769	.0865	0	− .6	
8.07	.4769	.0857	0	.2	
8.55	.5053	.1138	0	.5	
8.58	.5079	.1169	0	0	
8.58	.5079	.1171	0	−0.2	
8.88	.5250	.1329	0	−2.0	
9.26	.5479	.1525	0	−2.1	
9.87	.5839	.1743	0.7	1.8	
10.40	.6157	.1930	.4	1.9	0.03
10.68	.6313	.2029	.2	0	
10.97	.6483	.2129	0	0	
11.49	.6795	.2266	0	1.1	
11.86	.7007	.2400	0	−1.7	

The oxidation of the other substance mentioned, 3,4-diamino-1-naphthol, gave satisfactory titrations only in the limited region of PH 6–9, and as a matter of convenience the results have been included in Table II. In the neutral and weakly alkaline media the E_n:PH has the same characteristic 0.06 slope noted above and, although the evidence here is less extensive, it seems just as definite in pointing to the amino-quinone-imine, IVa, as the predominant tautomer, rather than the hydroxyquinonedi-imine, IVb.



IVa IVb

While the two oxidants just discussed are stable only in neutral or alkaline solutions and are not known in the solid state, the aminonaphthoquinone-imine obtained by the oxidation of 2,4-diamino-1-naphthol is completely stable over the entire PH range (at 25°) and it has been known for many years both in the free state[9] and in the form of the beautifully crystalline, fiery red monohydrochloride.[10] As noted by O. Miller,[11] the one basic center in the molecule is very strongly polar and thus it must be the imino group, rather than the primary amino group attached to the quinonoid nucleus, which is responsible for salt-formation. The hydrochloride thus must have the structure of either Va or Vb.

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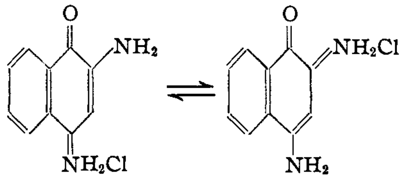
(9) Martius and Griess, *Ann.*, **134**, 377 (1865).

(10) Graebe and Ludwig, *ibid.*, **154**, 318 (1870).

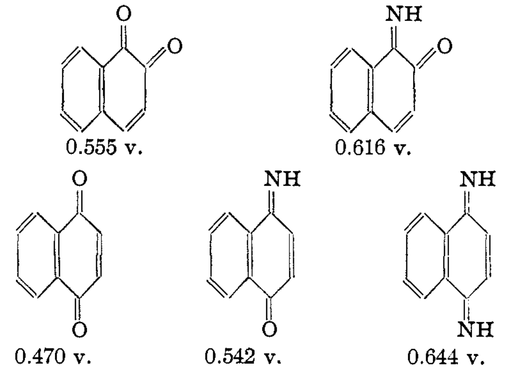
(11) Miller, *J. Russ. Phys.-Chem. Soc.*, **45**, 580 (1913).



Va Vb

The potentiometric results for this compound and its reductant are recorded graphically in Fig. 2. The character of the curve is such as to reveal one basic group of the oxidant and two basic groups and one acidic group of the reductant. Since, however, the two possible tautomers are both aminoquinone-imines, the equation given applies equally well to either form and the potential curve reveals nothing of the composition of the possible equilibrium mixture. A distinction between the two tautomeric forms thus cannot be made here as in the cases cited above. Whatever the structure may be it appears that the aminonaphthoquinone-imine in question is a very strong base and it is comparable in this respect with ammonia, the ionization constant (in the acidic sense) being 1.36×10^{-9}. The substance is a much stronger base than *p*-benzoquinone-imine, for which a constant of 1.2×10^{-4} was found,[1] or, in so far as can be judged, than any of the other oxidants included in the present study. On the basis of purely circumstantial evidence it would appear that the unusual stability of this quinone-imine is in some way connected with its strongly polar character, but it is not at all clear what particular structural feature so distinguishes the compound in this latter respect. As for the stability, particularly to hydrolysis by acids, it is a remarkable fact that of all of the naphthoquinone-imines and di-imines and their amino or hydroxyl derivatives, the only ones which exhibit a stability comparable to the substance under discussion are all derivatives of that substance, namely, the 5, 7 and 8-amino derivatives[12] and the 7-sulfonic acid.[13] Some additional observations regarding the interesting aminonaphthoquinone-imine are given in the Experimental Part.

The Relationship between Structure and Potential.—The present results furnish the material for some interesting comparisons, the first of which is that between the naphthoquinones and their imino derivatives. The pertinent data are assembled in the accompanying chart.[14] The replacement in a naphthoquinone of an oxygen atom in the α-position by an imino



NORMAL POTENTIALS IN AQUEOUS SOLUTION AT 25°

group results in an increase in the normal potential amounting to 61 mv. in the ortho series and 72 mv. in the para series. In concordance with the first of these figures it is found that the 1-imino derivative of 1,2-napthoquinone-4-sulfonic acid is 63 mv. higher in potential than the parent compound. A second substitution of the type indicated (in the para series) produces an even greater effect, the increase in potential in this case being 102 mv. In the benzoquinone series the relationships are similar but the effect of the substitution is less pronounced, being 29 mv. for the first imino group and (in alcoholic solution) 50 mv. for the second one. β-Naphthoquinone

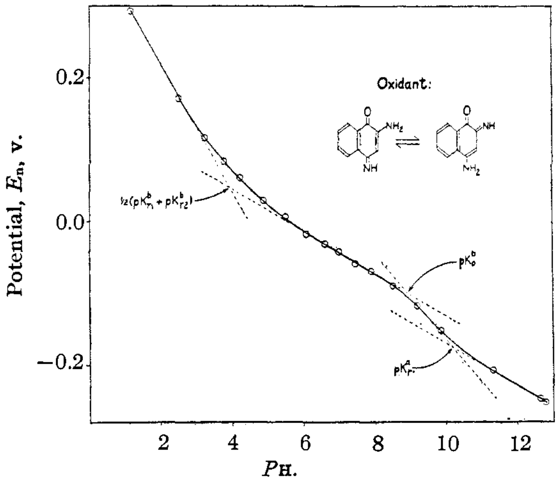


Fig. 2.—System from 2,4-diamino-1-naphthol (25°). Constants found: E_0, 0.4260 v. $K^b_{r_1}$, 2.00×10^{-5}. $K^b_{r_2}$, 7.20×10^{-4}. K^a_r, 6.61×10^{-11}. K^b_0, 1.32×10^{-9}. Electrode equation: $E_n = E_0 + E_h + 0.02956 \log [1 + [H^+]/K^b_{r_1} + [H^+]/K^b_{r_1}K^b_{r_2} + K^a_r/[H^+]] - 0.02956 \log [1 + [H^+]/K^b_0]$.

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[12] Kehrmann, *Ber.*, **31**, 2424 (1898); **33**, 3282 (1900); **34**, 1226 (1901).

[13] Lauterbach, *ibid.*, **14**, 2030 (1881).

[14] The value for α-naphthoquinone is that of La Mer and Baker, THIS JOURNAL, **44**, 1954 (1922).

is higher in potential than the α-isomer by 85 mv. in aqueous solution and by 92 mv. in alcoholic solution. The difference of 74 mv. between the corresponding quinone-imines is thus of the same order of magnitude.

The second point of interest is the effect of an amino group on the potential of a quinone. Such a substituent lowers the potential of α-naphthoquinone by 187 mv. and that of β-naphthoquinone by 229 mv. That the marked divergence of the two figures is not purely accidental but reflects a fundamental difference in the susceptibility of the two quinone structures to the modifying influence of substituents is indicated by a comparison of the amino derivatives of α- and β-naphthoquinone-1-imine. Thus the difference in potential between α-naphthoquinone-1-imine and its 2-amino derivative, IVa, is 160 mv.; for β-naphthoquinone-1-imine and the 4-amino derivative IIIb the difference is 225 mv. Indeed a direct comparison of the isomers IVa and IIIb is enlightening. The one with the orthoquinonoid structure is only 9 mv. higher in potential than the para isomer, while for the unsubstituted quinone-imines the difference is 74 mv. The greater influence of an amino group on the orthoquinonoid nucleus nearly compensates for the fact that this, *per se*, is the more active structure. A similar if less pronounced difference in the effect of substituents on the α- and β-naphthoquinones is discernible in the results for the sulfonic acid derivatives[3] and for the isomeric alkoxynaphthoquinones.[2]

From the results for the α-naphthoquinone derivatives it can be seen that a hydroxyl group attached to the quinonoid nucleus lowers the potential by an amount (119 mv.) which is only 58% of the effect of a similarly situated amino group. An interesting demonstration of the regularity of such results is the fact that although substituents influence the potential much less when they are situated in a benzenoid, rather than a quinonoid, ring the relationship between different substituents remains essentially the same. Thus a hydroxyl group in the 3-position of phenanthrenequinone has an effect (53 mv.) which is 54% that of a primary amino group in the same position (98 mv.).[15]

Theoretical Aspects of the Tautomerism.—It has been shown[2] from thermodynamical considerations that in an equilibrium mixture of two tautomeric forms of a given oxidant, either in the presence or absence of the common reductant, the position of the equilibrium is dependent upon the potentials of the two tautomers. For the general case of solutions at the point of half-reduction and at any acidity the relationship is expressed by the equation

$$\log K = (E^{\beta}_{n} - E^{\alpha}_{n})/0.02956$$

$$\text{where } K = [\alpha\text{-tautomer}]/[\beta\text{-tautomer}]$$

If the difference in potential amounts to 60 mv., then the tautomer of lower potential will constitute over 99% of the total. In those cases in which it has been possible to form reliable if approximate estimates of the relative potentials of the two tautomers, only one exception[16] has been found to the rule that the predominant tautomer is the one of lower reduction potential.

The present series of compounds affords a particularly fruitful field for further study of the applicability of the theoretical principle. In four cases it has been possible from an analysis of the E_n:P_H curve to determine that one or the other tautomer is practically the only species present in certain rather wide regions of P_H, and this more stable form may be either a quinone or a quinone-imine, it may contain hydroxyl or amino groups as substituents, and it may belong to either the ortho or the para quinonoid series. With such a diversification of types it would be quite significant if the stable tautomer were in each case the one of lower potential. While there is no direct experimental method of determining if this is the case, the knowledge of the relationship between potential and structure has advanced sufficiently far to warrant the use of estimated potentials.

Perhaps the clearest case is that of the tautomers represented above by the formulas IIIa and IIIb, either of which might be formed in the oxidation of 1,4-diamino-2-naphthol. The substance IIIa would be expected to be lower in normal potential than 1,4-naphthoquinonedi-imine by an amount corresponding to the effect of a hydroxyl group on the potential of the corresponding quinone, and the value of E_0 then would be 0.525 v. Substance IIIb may be regarded as derived from amino-β-naphthoquinone by the substitution of an imino group for oxygen at position 1, and the potential predicted on this basis is 0.387 v. In the limited P_H region actually investigated the difference between the two E_n values would be expected to be nearly as great

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[15] Fieser, This Journal, **51**, 3101 (1929).

[16] Fieser and Dietz, *ibid.*, **53**, 1128 (1931).

as that between the two normal potentials. Purely on the basis of these speculations substance IIIb would be expected to be the more stable tautomer and to have the normal potential indicated; the experimental results show that the oxidant does have this structure and that the potential is 0.391 v. The existence of the substance in question in what ordinarily would be the more active, or less stable, ortho-quinonoid condition is easily understandable; this feature is more than offset by the fact that IIIb is a mono- rather than a di-imine and it carries as substituent the amino group, rather than the less powerful (in the potential-lowering sense) hydroxyl group.

With the isomeric substance or substances obtained from 3,4-diamino-1-naphthol and represented in formulas IVa and IVb, every consideration points to the aminoquinone-imine as the tautomer of lower potential; it is *p*-quinonoid, it is a mono- rather than a di-imine, and it contains the amino rather than the hydroxyl group. In purely qualitative terms it is easy to see that the hydroxy-*o*-quinonedi-imine IVb would have a decidedly higher potential, but an exact estimation is not possible in the absence of information concerning 1,2-naphthoquinone-di-imine. It is perhaps safe to say that the figure would be at least as high as 0.600 v. and there can be little doubt that it would be inordinately higher than the value of 0.382 v. actually found for IVa.

The case of amino-α-naphthoquinone (Ia) and its tautomeric form, Ib, is best treated qualitatively inasmuch as the quinone-imine from which Ib is derived has not been characterized. There are, however, three structural features which would tend to favor the first tautomer and it is clear that the tautomer actually found to be the more stable (Ia) must also be the one of lower potential. On the assumption that there is no difference between the 1- and 2-imines of β-naphthoquinone, Ib should have a potential of approximately 0.497 v. The value is so much above that found (0.283 v.) that it is understandable that the potentials of the two tautomers apparently do not approach each other sufficiently closely in any region of *P*H to produce a noticeable change in the composition of the equilibrium mixture.

With the isomeric tautomer pair represented in the formulas IIa and IIb given above the situation is materially different from any thus far discussed. There are two factors favoring a lower potential for substance IIa, for this is an amino-quinone rather than a hydroxy-quinone-imine; but the less active *p*-quinonoid structure of tautomer IIb to some extent compensates for these differences. From such qualitative considerations it would be expected that the difference in normal potential would be less here than for any of the other tautomer pairs considered. Actually the aminoquinone form (IIa), or β-tautomer, has been found to have a normal potential of 0.326 v. (E_0), while for the α-tautomer it is possible to make a reliable estimation from the potential of α-naphthoquinone-imine and the known effect of a hydroxyl group on the potential of α-naphthoquinone. This gives a value for E_0^α of 0.423 v. The difference is sufficiently great to explain the fact that in solutions in which neither oxidant is ionized, no detectable amount of the α-tautomer is present in the equilibrium mixture.

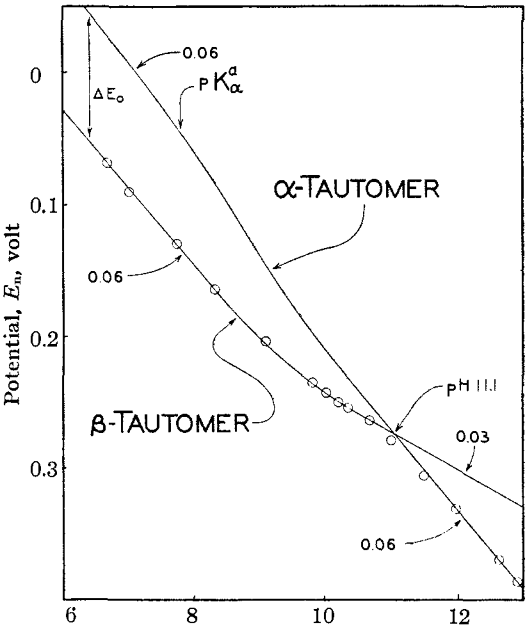

Fig. 3.—Theoretical curves for the two tautomeric forms of amino-β-napthoquinone. (The points are experimental.)

It has been found however that the α-tautomer does predominate in strongly alkaline solutions, and it remains to be seen if this behavior is consistent with the theoretical picture which has been presented. It thus becomes necessary to consider not just the potentials referred to the undissociated components of the systems but the variation of potentials with *P*H. The E_n:*P*H curve for the β-tautomer has been given in Fig. 1; a part of the curve is reproduced again in Fig. 3 with the

0.03 slope continued up to P_H 13 according to the demands of the electrode equation. In the alkaline range the experimental points do not fall upon this curve but form a straight line with the 0.06 slope, and this represents a portion of the curve for the α-tautomer. In the region in question the electrode equation for this tautomer may be written as follows

$$E_0^\alpha - 0.02956 \log K_\alpha^a = E_n^\alpha - E_h - 0.02956\ K_r^a$$

Since K_r^a is known (Table V), and since an average value for $(E_n^\alpha - E_h)$ can be obtained from the experimental results, it is possible to evaluate the quantity $(E_0^\alpha - 0.02956 \log K_\alpha^a)$. Neither of these constants can be determined experimentally, but if E_0^α is assumed to have the value estimated above, K_α^a is found to be equal to 1.58×10^{-8}. Using this value as the best approximation possible for the acidic dissociation constant of the α-tautomer, a theoretical E_n:P_H curve has been constructed for the α-tautomer, as shown in Fig. 3. The curve given is of course only an approximation, but its upper portion is subject to some displacement without greatly altering the general situation. The dispositions of the two curves are such as to make it possible for the β-tautomer to have the lower E_n value in neutral solutions but not in the strongly alkaline region.

From the foregoing analysis it is evident that the theory developed is quite generally applicable to the series of systems here considered, and that it serves as an accurate guiding principle in arriving at an understanding of this type of tautomerism. It should be specifically noted, however, that a reliable distinction between two tautomeric forms can be made only when the estimated difference in potential is large enough to eliminate the uncertainty of the calculated potentials. Thus we shall refrain from any attempt to define the predominant tautomer in the cases of the aminonaphthoquinone-imine Va or Vb, and of the aminoquinonedi-imine formed on the oxidation of 1,2,4-triaminonaphthalene.

Experimental Part

1. Preparation of Materials[17]

Hydrochlorides of 1,2- and 1,4-Aminonaphthol.—Completely pure, colorless samples of these substances were obtained by crystallization from an acid solution in the presence of 1–2% of stannous chloride. This serves as a highly efficient antioxidant and protects the substances even in a boiling solution or during a slow crystallization, and at the low concentration the reagent remains entirely in the mother liquor. This method of crystallization has been extremely useful in the purification of many other substances which are sensitive to oxidation, and it has made possible a considerable improvement in the preparation of the two aminonaphthols as well as of the corresponding quinones. The procedures will be described in a later paper.

3,4-Diamino-1-naphthol.—Kehrmann and Hertz[18] reduced the 1-oxime of 2-amino-1,4-naphthoquinone with stannous chloride and obtained 2,4-dihydroxy-1-naphthylamine. Suspecting that the hydrolysis of the amino group was the result of the use of an acidic medium, we carried out the reduction in a solution of the oxime in cold alkali by means of sodium hydrosulfite. The product, which indeed proved to be a diamine, was dissolved in dilute hydrochloric acid containing a trace of stannous chloride and crystallized as the dihydrochloride in the presence of an excess of acid. The substance was obtained in the form of small, not quite colorless, needles.

Anal. Calcd. for $C_{10}H_{12}ON_2Cl_2$: C, 48.59; H, 4.90. Found: C, 48.75; H, 5.19.

On oxidation of the substance in acid solution with ferric chloride 2-amino-1,4-naphthoquinone was produced in quantitative yield. Acetylation in aqueous solution gave the alkali-soluble diacetate which, however, is only slightly soluble in organic solvents and is not a suitable derivative for characterization. It thus was converted into the *triacetate* by boiling with acetic anhydride and pyridine. The material soon dissolved and the product then separated in a crystalline condition. It crystallized from glacial acetic acid in the form of clusters of small needles and melted with decomposition at 270–275°.

Anal. Calcd. for $C_{16}H_{16}O_4N_2$: C, 63.97; H, 5.37. Found: C, 64.55; H, 5.37.

1,2,4-Triaminonaphthalene.—It was hoped that this substance could be obtained by converting 2-amino-1,4-naphthoquinone-4-imine into the 1-oxime and reducing the product in a neutral or alkaline solution, but the oxime itself could not be obtained. On heating a solution of the hydrochloride of the imine (2.1 g.) with hydroxylamine hydrochloride (1.5 g.) and sodium acetate crystals (2.8 g.) on the steam-bath, a granular yellow product soon separated. This on rapid crystallization from alcohol was obtained as a yellow, micro crystalline product which appears to be *2-amino-1,4-naphthoquinone-4-oxime*.

Anal. Calcd. for $C_{10}H_8O_2N_2$: C, 63.81; H, 4.29. Found: C, 63.73; H, 4.49.

The evidence for the structure assigned is that on reduction with sodium hydrosulfite in an alkaline solution the substance is converted into 2,4-diamino-1-naphthol, which was identified as the di- and tri-acetate and by oxidation to the original aminoquinone-imine. We are thus of the opinion that in the reaction of the quinone-imine with hydroxylamine it is the imino group which is oximated.

The desired triamine was thus prepared from the less readily available 2,4-dinitro-1-naphthylamine.[19] The crude, moist amine obtained by the hydrolysis of 11 g. of the acetate was heated at the boiling point with a

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[17] By L. F. Fieser.

[18] Kehrmann and Hertz, *Ber.*, **29**, 1415 (1896).

[19] Morgan and Evens, *J. Chem. Soc.*, **115**, 1129 (1919).

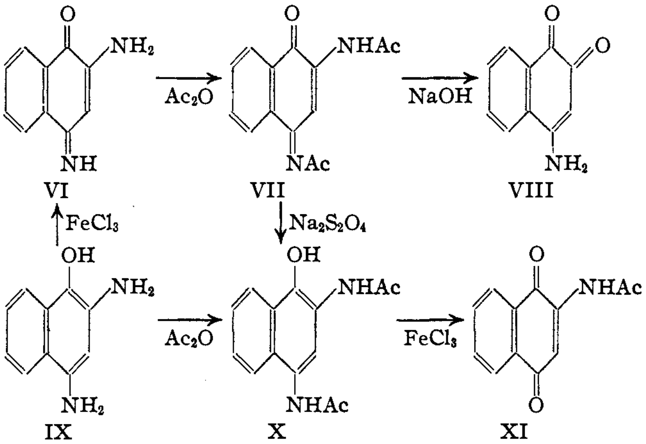
solution of 60 g. of stannous chloride in 60 cc. of concentrated hydrochloric acid until the material had all dissolved to give a brown solution. On adding 100 cc. of concentrated hydrochloric acid and cooling well a rather brown, crystalline product was precipitated. This formed good, nearly colorless needles on a further crystallization in the presence of a trace of stannous chloride; yield, 4.8 g. Further crystallizations yielded colorless needles which turned slightly pink on drying. The salt proved to be the **dihydrochloride.**

Anal. Calcd. for $C_{10}H_{13}N_3Cl_2$: C, 48.78; H, 5.32. Found: C, 49.01, 49.19; H, 5.13, 5.13.

The substance forms a very slightly soluble triacetate which was not obtained in a crystalline condition, and it yields highly colored condensation products with benzil and with phenanthrenequinone. It is converted by ferric chloride into 2-amino-1,4-naphthoquinone-4-imine, which was identified as the diacetate.

Other Compounds.—The following substances were prepared according to known methods and crystallized from acid solution in the presence of a small quantity of stannous chloride: 2,1-aminonaphthol hydrochloride,[20] colorless plates; 2,4-dihydroxy-1-naphthylamine hydrochloride,[21] long, colorless needles; 1,4-diamino-2-naphthol dihydrochloride,[18] fibrous, colorless needles; 1,4-naphthylenediamine dihydrochloride,[22] slightly pink needles. β-Naphthohydroquinone was obtained by adding a solution of 10 g. of sodium carbonate and 25 g. of sodium hydrosulfite to a suspension of the quinone from 10 g. of aminonaphthol hydrochloride in 200 cc. of water at 30°. Nearly colorless crystals were soon formed, and the product was crystallized from water containing stannous chloride and hydrochloric acid and formed colorless plates melting at 108°.

2. Reactions of 2-Amino-1,4-naphthoquinone-4-imine (or Tautomer).[17]—The preparation of this compound was greatly simplified by carrying out the reduction of Martius yellow by means of sodium hydrosulfite, so that the quinone-imine is now a very readily available substance. The acetylation of the imine, in the form of the hydrochloride, was first studied by Meerson,[23] who obtained a substance melting at 178° which he regarded as the diacetate, although his analyses diverged widely from the expected figures. Kehrmann and Täuber[6] repeated the experiment and obtained in place of Meerson's diacetate a mixture of the monoacetates of the two aminonaphthoquinones. O. Miller[24] obtained a diacetate melting at 187° from a specially dehydrated sample of the starting material and attributed the experience of the other workers to the disturbing influence of water of hydration. We had no difficulty in preparing a nicely crystalline, yellow diacetate melting at 189° in nearly theoretical yield from the crude air-dried hydrochloride, and the only precaution found necessary was to avoid overheating the reaction mixture. The identity of the reaction product is fully established by the following transformations.



The diacetate, which may be represented by Formula VII, yields the known triacetate of IX on reductive acetylation, and it is converted quantitatively on reduction into the diacetylaminonaphthol, X. It is a matter of interest that the latter compound, which apparently hitherto has not been isolated, does not yield on oxidation the substance from which it is obtained by reduction, but rather acetylamino-α-naphthoquinone, XI. Compound VII is not an intermediate in the reaction, for it is not subject to hydrolysis under the conditions used. The oxidation of X, which proceeds quantitatively, probably involves a free radical mechanism. A similar inference may be made regarding the oxidation of 4-acetylamino-1-naphthol to di-α-naphthoquinone.[25]

It was found possible to improve the established method of preparing the acetate XI, and hence of the amine obtainable from it, by acetylating IX in aqueous solution according to the excellent method of Lumière and Barbier,[26] and proceeding as indicated in the chart. The standard method of preparing amino-β-naphthoquinone, VIII, was also improved for it was found that this quinone is the exclusive product of the hydrolysis of the diacetate VII with alcoholic alkali. The usual method, which consists in the hydrolysis of VI with ammonia and which gives a mixture of the two isomeric aminonaphthoquinones, has been regarded[27,11,24] as a reaction furnishing evidence concerning the tautomeric composition of solutions of the aminonaphthoquinone-imine; but it appears to us that the formation of the two hydrolysis products may equally well be the result of the 1,2- and the 1,4-addition of water to a single tautomer such as VI. The conversion of a para to an ortho quinone structure by an addition reaction is by no means novel.[5]

Preparation of the Quinone-imine Hydrochloride.—A suspension of 50 g. of Martius yellow (technical sodium salt) in 1 liter of water at room temperature was stirred mechanically and 270 g. of sodium hydrosulfite was added in the course of fifteen minutes. The material at first largely dissolved to give a red solution from which the

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(20) Liebermann and Jacobson, *Ann.*, **211**, 55 (1882).

(21) Kehrmann and Mascioni, *Ber.*, **28**, 345 (1895).

(22) Cobenzyl, *Chem. Zentr.*, I, 1737 (1925).

(23) Meerson, *Ber.*, **21**, 1195, 2516 (1888).

(24) Miller, *J. Russ. Phys.-Chem. Soc.*, **45**, 1480 (1913).

(25) Ullmann, *Helv. Chim. Acta*, **9**, 442 (1926).

(26) Lumière and Barbier, *Bull. soc. chim.*, [3] **33**, 785 (1905).

(27) O. Miller, *J. Russ. Phys.-Chem. Soc.*, **42**, 1418 (1910).

diaminonaphthol soon separated as a tan crystalline precipitate, the temperature rising to 36°. After stirring further for fifteen minutes the mixture was cooled to 10° and the product collected. The free base is extremely sensitive to air-oxidation, and the filter cake was thus washed with a 1% sodium hydrosulfite solution and was not allowed to drain entirely free from this reagent until ready to be transferred quickly to a beaker containing 40 cc. of concentrated hydrochloric acid and 500 cc. of water. The substance dissolved rapidly on stirring and the solution after being filtered through a layer of decolorizing carbon was only slightly colored. A filtered solution prepared from 120 g. of ferric chloride crystals, 50 cc. of concentrated hydrochloric acid and 100 cc. of water by heating, and cooled by the addition of 200 g. of ice was then added, followed by 100 cc. of concentrated hydrochloric acid. The quinone-imine hydrochloride soon separated on cooling in the form of beautiful fiery red crystals which were washed with dilute acid and air-dried at room temperature. The yield was 31.5 g.; assuming a pure starting material this would represent a yield of 78%, but the actual yield is probably considerably higher. If 2,4-dinitro-1-naphthol is available as such, rather than as the sodium salt, it is most convenient to convert it for the reduction into the ammonium salt.

2,4-Di-(acetylamino)-1-naphthol (X).—Fifty grams of Martius yellow was reduced and the product converted into a filtered solution of diaminonaphthol dihydrochloride as described above. Forty cc. of acetic anhydride was dissolved in this solution (25°) by stirring and a cold, aqueous solution of 70 g. of crystalline sodium acetate and 1 g. of sodium hydrosulfite was then added all at once. The diacetate at first separated in an oily condition but on cooling and stirring it largely solidified to a granular white powder. The crude product (34 g.) was stirred with a cold solution of 25 cc. of 6 *N* sodium hydroxide solution in 400 cc. of water, adding a trace of sodium hydrosulfite to discharge a slight color. It dissolved rapidly and the solution, after being filtered by suction, was acidified with hydrochloric acid to reprecipitate the diacetate. After cooling the mixture thoroughly for one hour the colorless, granular solid was collected and dried; yield, 32.4 g. (64%, assuming the starting material to be pure). This material is quite pure and the melting point is not changed by crystallization. The substance tends to darken during crystallization unless oxidation is arrested by the use of a trace of stannous chloride and hydrochloric acid. After diluting a hot solution in glacial acetic acid with 4–5 volumes of hot water, large, colorless needles were slowly deposited; m. p. 225° with decomposition.

Anal. Calcd. for $C_{14}H_{14}O_3N_2$: C, 65.10; H, 5.47. Found: C, 65.10; H, 5.56.

The diacetate is converted on further acetylation into the known triacetate, m. p. 274°, and it may be prepared from the latter substance by digestion with cold, dilute alkali. If the alkaline solution is treated with an excess of hydrochloric acid, and if the solution is not too concentrated, a clear solution often results and the diacetate separates only after the lapse of several minutes, even though it is but sparingly soluble in water. The marked tendency of the compound to remain in supersaturated solution accounts for an erroneous observation recorded in the literature. Meerson[23] hydrolyzed the triacetate with alkali, acidified the solution and added ferric chloride, thus discovering the most satisfactory method developed for preparing acetylamino-α-naphthoquinone. Since he observed no precipitate in the acidified solution, Meerson thought that the intermediate was acetylamino-1,4-aminonaphthol, but it is now clear that the behavior noted was due to supersaturation rather than to the presence of a free amino group.

2-Acetylamino-1,4-naphthoquinone.—The above diacetate (32.4 g.) was dissolved in 175 cc. of hot glacial acetic acid, the solution was diluted with 100 cc. of hot water and treated with a filtered solution of 78 g. of crystalline ferric chloride and 25 cc. of concentrated hydrochloric acid in 300 cc. of water. The quinone separated in a very pure condition: yellow plates, m. p. 204°; yield, 25.7 g. (95%).

2-Amino-1,4-naphthoquinone.—It was our experience that the time specified by Meerson[23] for the acid hydrolysis of the acetate is much too long; following these directions we obtained chiefly hydroxynaphthoquinone. The following method is thus recommended. The acetylaminoquinone described above (25.7 g.) was treated with 51.4 cc. of concentrated sulfuric acid and stirred. There was considerable warming and the quinone rapidly dissolved to give a deep red solution. The mixture was heated for just fifteen minutes, poured into a large volume of water, and the precipitated quinone was collected and washed well with water. The product was quite pure; yield, 16.9 g. (82%). Samples crystallized from alcohol melted at 206°. The quinone dissolves in cold alcoholic alkali to give an intensely purple-colored solution from which the aminoquinone separates on dilution with water in a crystalline condition.

2 - Amino - 1,4 - naphthoquinone - 4 - imine Diacetate (VII).—A mixture of 15 g. of the quinone-imine hydrochloride, 15 g. of fused sodium acetate and 50 cc. of acetic anhydride was warmed to 70–80° and stirred well until the red crystals all had been converted into a crystalline, yellow solid. The mixture was poured into water, the product was collected and washed with water, followed by a small quantity of alcohol. The product was practically pure; yield, 16 g. (87%). Crystallization from alcohol gave canary-yellow, stout needles melting at 189°.

Anal. Calcd. for $C_{14}H_{12}O_3N_2$: C, 65.60; H, 4.72. Found: C, 65.33; H, 4.57.

The quinone-imine derivative was converted by reduction with sodium hydrosulfite in an alcoholic suspension into diacetylaminonaphthol, m. p. 225° (93% yield); while the triacetate, m. p. 274°, was obtained on treatment with zinc dust, sodium acetate and acetic anhydride (85% yield).

4-Amino-1,2-naphthoquinone.—Two grams of the diacetate of aminonaphthoquinone-imine was suspended in 20 cc. of alcohol containing 5 cc. of 6 *N* sodium hydroxide solution and the mixture was stirred in the cold until the yellow crystals had all dissolved to give a deep red solution (half an hour). After diluting with 70 cc. of water and filtering, the solution was acidified with acetic acid, when the aminoquinone separated as an easily filterable red powder; yield 1.2 g. (89%). The basic character of the substance is apparent from the fact that if the above solution is acidified with an excess of hydrochloric rather than acetic acid no precipitation occurs. The material was of as good quality as that prepared by the usual method. It formed the characteristic red needles on crystallization from water and it was fully identified through the preparation of the hydroquinone triacetate (m. p. 195°) as well as of the acetate and the hydroquinone of the acetate, and comparison with authentic samples.

3. E. m. f. Measurements[28]

After some experimentation the following procedure was adopted for the preparation of solutions of the easily oxidizable reductants in the absence of air. A weighed quantity of the reductant, usually 0.00675 mole, was placed in a hydrogenation bottle and a small glass cup containing 10 mg. of Adams catalyst was slid into the bottle. It was found necessary to keep the catalyst out of contact with the dry organic material, for otherwise ignition usually occurred on the admission of hydrogen. The bottle was connected through one opening in the stopper to a hydrogen tank fitted with a three-way valve, and a second opening carried a glass tube which could be thrust when desired to the bottom of the bottle, and which was provided at the lower end with an inverted funnel carrying a filter plate and paper. At the top of the tube a short section of rubber tubing made temporary connection to the delivery tube of a separatory funnel in which was placed 225 cc. of water. The water was swept with a stream of nitrogen and at the same time the bottle was evacuated. After a time hydrogen was admitted; the bottle was further evacuated, flushed with hydrogen and again evacuated. The water was then run in, the entrance tube was closed with a pinchcock, and hydrogen was admitted at a pressure of about 6 pounds. The sample soon dissolved on starting the shaking mechanism and in some cases the initial solution was perfectly colorless. Often, probably either because of a slight deterioration of the sample on drying or because of the presence of a trace of oxygen in the hydrogen, the solution was at first slightly pink or yellow. The color was soon discharged, however, after the catalyst had become activated, and a completely colorless solution was obtained in every case. The solution was then forced through the filter under hydrogen pressure into the reservoir of a protected buret, which had been swept with oxygen-free nitrogen.

When the oxidant of the system to be studied was obtainable in a pure condition the solution of the reductant was prepared by hydrogenating a weighed sample of the material suspended in the above volume of water containing a quantity of hydrogen chloride sufficient to neutralize any basic groups of the reductant. This was the procedure used for: the two aminonaphthoquinones, 2-amino-1,4-naphthoquinone-4-imine, hydroxynaphthoquinone.

For each titration 10 cc. of the solution of the reductant was run directly into the electrode vessel containing 190 cc. of buffer solution which had been freed of oxygen with a stream of nitrogen. Connection was made through a saturated potassium chloride bridge to a saturated calomel electrode whose potential was fixed by reference to 0.1 normal electrodes. Potassium ferricyanide served as a satisfactory titrating agent in all but a few instances, when molybdicyanide was employed. The total concentration of the organic system at half-oxidation was approximately 0.0014 molar in every case except that of β-naphthoquinone, when the concentration was just half that given and the stock solution of the reductant was made up to contain the 0.00015 mole required for each run in 25 cc. of solution.

The buffer solutions were for the most part 0.2 *M* in buffer salts and 0.1 *M* in potassium chloride, and they were of the following types: *P*H 0.3–2.5, HCl, glycine or citric acid; *P*H 3.2–4.9, phthalate or acetate; *P*H 5.5–6.1, citrate; *P*H 6.2–8.0, phosphate; *P*H 8–9, veronal; *P*H 8–9.3, borate (except for reductants containing hydroxyl groups in the ortho position); *P*H 9.8–10.4, glycine; *P*H 10.4–12.7, phosphate; *P*H 12.8, KOH. The values reported in the tables for the hydrogen-ion concentrations were determined by measuring the potential of a given buffer diluted with the volume of water which would be added up to the mid-point of a titration and containing where appropriate a quantity of aniline hydrochloride or of *m*-phenylenediamine hydrochloride equivalent to the reductant salt used.

The titrations require little comment. In every case the curves corresponded well with the theoretical curve for a two-equivalent oxidation. Where discontinuous titrations were required it usually was possible to determine the end-point by titration at some other acidity. The decomposition of the quinone-imines was found to follow the course of a monomolecular reaction, indicating that the reaction involved is probably one of hydrolysis, while the decomposition of 1,4-naphthoquinonedi-imine was found to be a pseudo bimolecular reaction with a velocity constant of 3.5×10^{-3}.

Summary

A potentiometric study has been made of the oxido-reduction systems from certain of the naphthoquinone-imines and di-imines and their hydroxyl and amino derivatives. The results obtained serve to extend the knowledge of the relationship between structure and potential and they furnish information regarding both the acidic or basic strength of hydroxyl or amino groups situated in the quinonoid nucleus, and the effect of these substituents upon the potential of the parent substance.

The most significant observations have to do with the tautomerism of the aminoquinones and quinoneimines. From the nature of the variation of potential with hydrogen-ion concentration it has been possible in four cases to determine which of the two possible structures represents the predominant tautomer. In the case of amino-β-naphthoquinone it has been found that the substance exists as an aminoquinone in all *P*H regions except that of extreme alkalinity, where a change to the hydroxyquinone-imine form takes place.

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[28] By M. Fieser.

In every instance the results appear to be in good accord with the theory that the tautomer of lower oxido-reduction potential is the one which will predominate in the equilibrium mixture.

CONVERSE MEMORIAL LABORATORY
CAMBRIDGE, MASS.

RECEIVED MARCH 31, 1934

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

The Mechanism of the Reaction of Dimethyl Sulfate with Arylmagnesium Halides

BY ARTHUR C. COPE[1]

The reaction of dimethyl sulfate with Grignard reagents furnishes a valuable method for the synthesis of methyl hydrocarbons. The discoverers of the reaction[2] represented it by the equation

$$(CH_3)_2SO_4 + RMgX \longrightarrow RCH_3 + CH_3OSO_2OMgX \qquad (1)$$

While the equation is still commonly written in this manner, the reaction has also been represented[3] as requiring two moles of dimethyl sulfate, one mole being utilized in the production of methyl halide

$$2(CH_3)_2SO_4 + RMgX \longrightarrow RCH_3 + CH_3X + (CH_3OSO_2O)_2Mg \qquad (2)$$

Evidence that two moles of the alkylating agent are necessary to complete the reaction is afforded by the work of Rossander and Marvel[4] and Gilman and Heck,[5] who found that alkyl halides (R′X) as well as alkyl hydrocarbons (R—R′) are formed through the reaction of alkyl *p*-toluene sulfonates with Grignard reagents (RMgX).

While the complete reaction (2) seems to be well established, there is little evidence as to its mechanism. In the case of alkyl sulfonates, when one mole of $CH_3C_6H_4SO_2OR'$ is used the products are R—R′, RH and R′X. Rossander and Marvel[4] explained the formation of the alkyl halide by a cleavage of the Grignard reagent at the Mg—X bond[6]

$$CH_3C_6H_4SO_2OR' + RMgX \longrightarrow R'X + CH_3C_6H_4SO_2OMgR$$

Hydrolysis of the new magnesium derivative produced in this manner would account for the formation of RH. Gilman and Heck[5] preferred to explain the formation of the alkyl halide by a reaction of the halomagnesium salt produced in the alkylation process

$$CH_3C_6H_4SO_2OR' + CH_3C_6H_4SO_2OMgX \longrightarrow R'X + (CH_3C_6H_4SO_2O)_2Mg$$

Hydrolysis of unreacted Grignard reagent would account for the formation of RH.

In this investigation an attempt has been made to determine the mechanism of the reaction of dimethyl sulfate with arylmagnesium halides. The Grignard reagents and dimethyl sulfate were allowed to react in equimolecular proportions, and then the yields of all of the products formed were determined by a method which is described in the experimental part. The data obtained are summarized in Table I.

Since two moles of dimethyl sulfate are required to complete the reaction (equation 2) a portion of the Grignard reagents was recovered. In three of the cases the recovered Grignard reagent contained much more basic magnesium than halogen; in other words, part of it was present as R_2Mg. Since the diarylmagnesium could hardly have been formed through reaction of the arylmagnesium halide with dimethyl sulfate, the presence of R_2Mg in the original Grignard reagent is established. Independent chemical evidence is thus obtained in support of Schlenk's conclusion[7] that Grignard reagents exist in the equilibrium: $2RMgX \rightleftharpoons R_2Mg + MgX_2$. The increase in the ratio of basic magnesium to halogen produced in the Grignard reagents through partial reaction with dimethyl sulfate must be attributed to a relatively rapid removal of magnesium halide from this equilibrium to form methyl halide. The results of experiments in which magnesium bromide and iodide were allowed to react with dimethyl sulfate substantiate the conclusion that the magnesium halides in equilibrium with the Grignard reagents are a principal source of the methyl halide, since methyl halides were pro-

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[1] National Research Fellow in Chemistry.

[2] Werner and Zilkens, *Ber.*, **36**, 2116, 3618 (1903); Houben, *ibid.*, **36**, 3083 (1903); **37**, 488 (1904).

[3] "Organic Syntheses," 1931, Vol. XI, p. 66.

[4] Rossander and Marvel, THIS JOURNAL, **50**, 1491 (1928).

[5] Gilman and Heck, *ibid.*, **50**, 2223 (1928).

[6] Such a cleavage had been postulated previously by Kenyon, Phillips and Turley, *J. Chem. Soc.*, **127**, 399 (1925).

[7] Schlenk and Schlenk, *Ber.*, **62**, 920 (1929).