CCCVII.—*The Determination of Dissociation Constants of Dihydric Mono- and Di-nitrophenols Electrometrically and Colorimetrically.*

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THE conductivities were determined by the Kohlrausch method in a gas-regulated thermostat which was maintained at 25·0° ± 0·05°. The cell constant, as determined by solutions of $N/10$- and $N/100$-potassium chloride and saturated calcium sulphate, was 0·298. The conductivity water had a specific resistance of 4—5 × 10^{-6} reciprocal ohm. The conductivities were corrected for that of the water by the usual method (Ostwald and Luther, "Physicochemical Measurements ") at the highest dilutions, when necessary. The trustworthiness of the apparatus was tested by determining the conductivity of acetic acid, with the following results :

At v =	16	32	64	128	256
$K \times 10^6$ =	18·33	18·56	18·47	18·36	18·50

The colorimetric measurements were carried out in a small colour comparator, in daylight, and in the manner already described (J., 1924, **125**, 2110; 1925, **127**, 2499).

The Preparation and Properties of the Compounds, and the Determination of their Constants.

2 : 6-*Dinitroquinol.*—The preparation and properties of this compound have already been described (J., 1924, **125**, 2110). The dissociation constant determined by Bader (*Z. physikal. Chem.*, 1890, **6**, 287), when multiplied by 10^{-2} in order to render it comparable with the more usual mode of expression, was $0·7 \times 10^{-4}$, at dilutions from 200 to 1600. Bader's value of λ_0, translated into modern units, is 376, whereas we find that λ_0 of the dinitro-acid is 380. It was decided to repeat the measurements of this compound for this reason and for others, among which were the circumstances that it was evidently sensitive to catalytic oxidation and that the purity of some of Bader's preparations had been questioned by subsequent workers (*e.g.*, Walker and Cormack, J., 1900, **77**, 5).

Solutions freshly made from the calculated weights of either the hydrated or the anhydrous compound were found to have the same conductivities. When they were allowed to stand in contact with the electrodes for some time, the colour changed from red to yellowish-brown, the conductivity altered, and the characteristic purple colour then no longer appeared on the addition of alkali. These changes are probably due to oxidation. The colour also changed when hydrogen was passed over the electrode, and finally a black precipitate appeared; thus reduction also probably takes place. Solutions were freshly made for each determination of conductivity, the dilutions being performed outside the cell, because it was soon evident that these changes in their first stages were accompanied by a diminution in the resistance in the more dilute, as well as in the more concentrated, solutions. Three independent series of measurements were first made, and the constants calculated in the usual manner.

	First series.				Second series.			Third series.	
v =	184	368	736	1472	203	406	812	562	1124
λ =	60·2	70·0	81·8	101	66·6	76·8	85·8	74	93·2
$K \times 10^4$ =	1·62	1·13	0·80	0·655	1·83	1·26	0·81	0·83	0·71

In the fourth series, measurements were made after 20, 40, and 60 secs., and the readings were extrapolated to zero time; for instance, in one case the resistances of the solution in the cell were 1975, 1940, and 1920 ohms, respectively. Hence, at zero-time the resistance was 2010 ohms and the constant $1·72 \times 10^{-4}$.

v =	221	442	884	1768
λ =	67·2	80	89·5	106·5
α =	0·177	0·211	0·236	0·280
$K \times 10^4$ =	1·72	1·27	0·824	0·614

There is thus an undoubted diminution of the constant with dilution, in the direction usually observed in the case of acids of medium strength, although 2 : 6-dinitroquinol is not sufficiently strong to be included in this class, which might, however, include the strongest of the acids investigated. In the case of 2 : 6-dinitroquinol, we suspect that the anomalous behaviour is connected with the transition into the second, or red, quinonoid form, for, at the p_H produced by the dissociation of the compound itself in water, this transition would have proceeded to a considerable extent. Pending an explanation, we have adopted a mean constant of $1 \times 10^{-4}, p_K = 4·0 \pm 0·2$, for comparison with the other compounds.

3 : 5-*Dinitropyrocatechol*.—This compound, as previously described (J., 1925, **127**, 2499), appears as bright yellow crystals, m. p. 164°. The conductivity of the solutions did not alter on standing in contact with the electrodes. Three series of readings gave :

At v =	890	1010	1010	1780	2020	2020	3560	4040	4040
λ =	149·5	162·5	160·0	190	204	200	228	243	243·5
$K \times 10^4$ =	2·88	3·17	3·09	2·80	3·10	2·92	2·54	2·8	2·8

The mean value of K is $2·9 \times 10^{-4}, p_K = 3·54$.

2 : 4-*Dinitroresorcinol*.—2 : 4-Dinitrosoresorcinol, prepared according to the method of Fitz (*Ber.*, 1875, **8**, 631), was treated with cold concentrated nitric acid (Kostanecki and Feinstein, *Ber.*, 1888, **21**, 3121) in a freezing mixture to minimise the formation of styphnic acid, any of which was removed by shaking with a large quantity of water. The nitro-compound appeared as light yellow crystals, m. p. 142°. The solution was quite stable in contact with the electrodes. Two series of measurements were made, in each of which a distinct diminution of the constant with increasing dilution was observed. Since this is by far the strongest acid of the series, we consider that this diminution may be due to the same causes as that found in the case of acids of medium strength.

	First series.						Second series.				
v =	190	380	760	1520	3040	6080	240	480	960	1920	7680
λ =	129	162	200	236	262	265	141·5	177	215	248	273
$K \times 10^4$ =	9·22	8·43	8·47	6·74	5·05	4·70	9·29	8·47	7·73	6·44	2·69

In accordance with the usual practice, we have excluded values obtained at a degree of primary ionisation greater than 0·5 ($v > 700$). The mean value of K is $8{\cdot}85 \times 10^{-4}$, $p_K = 3{\cdot}05$.

The compound is colourless in acid solution, and full yellow from about p_H 6·65. There is no further colour change in more strongly alkaline solution up to p_H 12. The colorimetric degrees of transformation were investigated by the methods which are described in the two former papers (*loc. cit.*). The values were found, however, to vary with the p_H of the standard buffer solution containing the partly transformed compound, thus

At p_H =	3·69	3·37	4·2
p_K =	4·09	3·85	4·3

None of the other compounds investigated shows such variations. The colorimetric constant can therefore only be roughly defined as 3·9 ± 0·4—the mean of many determinations at various concentrations. The colour change is very gradual; thus no difference in colour between solutions of p_H 4·77 and 5·07, each containing 8 drops of $M/20$-solution of the compound (in alcohol), can be detected by visual matching.

4 : 6-*Dinitroresorcinol.*—This compound, prepared as already described (*loc. cit.*, 1925), forms yellow prisms, m. p. 214·5°. It is the least soluble of all the compounds investigated. The solutions were quite stable when in contact with the electrodes. The bridge settings were not quite so accurate at these high dilutions and resistances. The last value was not used in calculating the constant, since the corresponding degree of ionisation was 0·68.

v =	2560	5180	5180	10,360
λ =	163	198	188	257
$K \times 10^4$ =	1·22	1·09	0·94	1·39

The mean value of K is $1{\cdot}05 \times 10^{-4}$, $p_K = 3{\cdot}98$.

The solubility of the compound was found to be 0·0781 g. per litre by means of a conductivity titration, using a method which we hope to describe in a further communication.

The mobility of the dinitro-anion was determined by means of the monosodium salt. An $N/61{\cdot}9$-solution ($v_1 = 61{\cdot}9$) was diluted in steps of 2, the corresponding values of λ_1, etc., being treated by the well-known formula derived from the graph of λ and $\sqrt[3]{C}$ in order to obtain λ_0 (Kohlrausch, "Das Leitvermögen der Elektrolyte").

λ_1	λ_2	λ_4	λ_8	λ_{16}	λ_{32}
68·4	72·1	74·9	76·75	78·6	79·9

Hence $\lambda_0 = 2\lambda_8 - \lambda_1 = 85{\cdot}1$, etc.; the mean value was 85·0. The same results were also treated by the method of Ferguson and Vogel (*Phil. Mag.*, 1925, **50**, 971). In the equation

$$\log \delta\lambda = n \log C - \log B(1 - r^n),$$

in which C is the concentration, $\delta\lambda$ the difference in λ brought about by the dilution in the common ratio "r" (in this case 2), the constants n and B were found to be $n = 0{\cdot}437$, $B = 90{\cdot}9$. Hence λ_0 from the individual values of $\delta\lambda$ was 83·08 (82·8—83·2). The compound therefore behaves quite normally like a salt of a strong base and a strong acid. For several reasons we have preferred the value of λ_0 as given by the usual method. Combining this with the limiting mobility of $Na^{\bullet} = 51$, we find that of the anion to be 34, and that of the free monobasic acid 381.

Nitroquinol.—The sample consisted of dark red crystals, m. p. 128° (*loc. cit.*, 1924). The solutions, like those of dinitroquinol, changed in conductivity on standing in contact with the electrodes. Dilutions were therefore made outside the cell, and measurements were taken quickly. The two values of λ refer to two experiments at each dilution. The conductivity can be restored to nearly its original value by passing hydrogen over the electrodes.

v =	127	248	254	496	508
λ =	4·2 (4·74)	6·07 (6·31)	5·7 (7·25)	9·88 (10·2)	7·06 (7·74)
$K \times 10^6$ =	0·981	1·13	0·92	1·41	0·701

The values in brackets are given as showing the variability introduced by a slight delay in taking measurements. The constant is calculated from the lowest values of λ in each case. The mean constant is $1{\cdot}01 \times 10^{-6}$, $p_K = 6{\cdot}0$.

3-*Nitropyrocatechol.*—This was prepared by a modification of the method of Weselsky and Benedickt (*Monatsh.*, 1882, **3**, 386). The mixture of the 3- and 4-isomerides with unchanged pyrocatechol was distilled with steam. The distillate, containing the pyrocatechol and the 3-isomeride, was extracted with ether. The residue from this extraction was further extracted with boiling light petroleum. The 3-isomeride was obtained as bright yellow needles, m. p. 86°. Solutions kept in contact with the electrodes change in conductivity: the change is accelerated by passing oxygen and retarded by passing hydrogen. The precautions already mentioned were taken.

	First series.				Second series.	
v =	65·4	130·8	261·6	523·2	184	736
λ =	4·15	6·08	7·42	10·3	6·1	17·4
$K \times 10^6$ =	1·87	1·99	1·50	1·45	1·45	3·01

The mean value of K is $1{\cdot}88 \times 10^{-6}$, $p_K = 5{\cdot}73$.

The compound is colourless in acid solution, and full yellow at p_H 7·8—10·0. At higher values of p_H, there is a second change, to red-brown, becoming purple at about p_H 13—14. The colorimetric constants were determined by the methods already described:

$$_1K = 1 \times 10^{-5},\ p_{K_1} = 4{\cdot}95;\ _2K_c = 0{\cdot}93 \times 10^{-11},\ p_{K_2} = 11{\cdot}03.$$

4-Nitropyrocatechol.—The method of Weselsky and Benedickt gives a product mixed with tarry matter. A more satisfactory method is that of Benedickt (*Ber.*, 1878, **11**, 362). The product when recrystallised from hot benzene is light brown, m. p. 173°. The conductivity of the solutions increased when they were in contact with the electrodes; the lower value of λ was therefore used in calculating the constants.

v =	48·1	51·5	96·2	192·4	384·8
λ =	1·51 (1·77)	1·72	1·97 (2·14)	2·25 (2·49)	5·22 (6·00)
$K \times 10^7$ =	3·33	4·05	2·83	1·85	5·02

The mean value of K is $3{\cdot}52 \times 10^{-7}$, $p_K = 6{\cdot}45$.

The compound is faintly yellow even in acid solution. It changes to red and ultimately to purple with increasingly alkaline solutions.

The constant of the first colour change was determined as already described. The second colorimetric constant was determined by comparison of a tube containing 5 drops at p_H 7·25 (full yellow) behind one containing 5 drops at p_H 13·76 (red) with one containing 10 drops, which matched when p_H was adjusted to 10·96. In another experiment, 8 drops of the solution of 4-nitropyrocatechol in a known p_H (10·64), were matched by 2 drops (in red solution) plus 6 (in yellow). The mean constants are $K_1 = 2{\cdot}8 \times 10^{-6}$, $p_{K_1} = 5{\cdot}56$; $K_2 = 1{\cdot}1 \times 10^{-11}$, $p_{K_2} = 10{\cdot}96$. An $M/20$-alcoholic solution was used.

2-Nitroresorcinol.—The method of preparation and the determination of the colorimetric constants have already been described (*loc. cit.*, 1925). The compound appeared as bright red crystals which melted sharply at 83·5°. Since the compound and its sodium salt are quite stable in solution, the latter was used in the determination of the mobility of the mononitro-anion, in the manner described above. Solutions were diluted in the cell, each dilution being two-fold, and the initial dilution, corresponding to λ_1, being 33·8.

λ_1	λ_2	λ_4	λ_8	λ_{16}	λ_{32}
66·2	69·7	72·9	75·9	77·1	78·8

Hence $\lambda_0 = 2\lambda_8 - \lambda_1 = 85{\cdot}6$, etc., the mean of the values of λ_0 being 84·9.*

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* The degree of hydrolysis is inappreciable at all dilutions except the highest (v = *ca.* 1000). Taking K as $1{\cdot}6 \times 10^{-6}$, we find by the usual formula that the degree of hydrolysis is $2{\cdot}24 \times 10^{-3}$. The difference between λ_0 of sodium hydroxide and the sodium salt of the acid is 192 − 33·5 = 158·5. Therefore, if these two electrolytes were equally dissociated, the repression of the hydrolysis would diminish the value of λ by

$$(2{\cdot}24 \times 10^{-3} \times 158{\cdot}5) \times 78{\cdot}8/85 = 0{\cdot}33.$$

Hence $\lambda_{32} = 78{\cdot}47$ and $2\lambda_{32} - \lambda_4 = 84{\cdot}05$.

The graph of λ against $\sqrt[3]{C}$ gives λ_0 as 84—85, and we use 84·5 as the most probable value. Hence the mobility of the anion is 33·5, and λ_0 of the free acid is 380·5. The conductivity of the acid remained constant when the solutions were kept in contact with the electrodes.

	First series.		Second and third series.			
v =	700	1400	288	349	576	1152
λ =	12·5	17·8	7·85	8·5	11·45	15·75
$K \times 10^6$ =	1·65	1·67	1·53	1·48	1·65	1·56

The mean value of K is $1{\cdot}59 \times 10^{-6}$ ($p_K = 5{\cdot}80$), which is only about $\frac{1}{10}$ of that found by Bader ($1{\cdot}29 \times 10^{-5}$).

The preparation showed all the usual criteria of purity, however, and the solutions were made up with the usual precautions.

4-*Nitroresorcinol.*—4-Nitrosoresorcinol, prepared according to Henrich (*Ber.*, 1902, **35**, 4193), was oxidised with alkaline hydrogen peroxide (Borsche and Berkhout, *Annalen*, 1904, **330**, 106). In order to obtain any yield at all, it is essential (*a*) that the hydrogen peroxide should be not weaker than 3%, and (*b*) that the solution should be kept alkaline as long as possible, *i.e.*, after the reaction is over it must be kept boiling for at least ½ hour and concentrated to a convenient bulk, then acidified, and extracted with ether. The product after recrystallisation from hot water is the semihydrate, yellow crystals, m. p. 82°. It may be quickly dehydrated at 70° giving the anhydrous compound, m. p. 115°.

	First series.		Second series.		
v =	69	138	186	372	744
λ =	3·11	4·37	5·56	7·35	11·08
$K \times 10^6$ =	0·98	0·97	1·16	0·99	1·11

The mean value of K is $1{\cdot}04 \times 10^{-6}$ ($p_K = 5{\cdot}98$), which agrees fairly well with Bader's value, $1{\cdot}2 \times 10^{-6}$.

The compound is colourless in acid solution, and completely yellow between p_H 9 and 10. There is no further change in colour in more alkaline solution. The mean value of the first, and only, colorimetric constant is $K_1 = 1{\cdot}55 \times 10^{-9}$, $p_K = 8{\cdot}81$.

Discussion of Results.

It was not expected that the constants of compounds which undergo tautomeric changes would be as uniform as those of normal electrolytes; these changes are probably the cause of the "drifts" which were found in several cases. The irregularities which are found in some cases have been already traced to irreversible or only partly reversible changes brought about by the catalytic activity of the electrodes. The constant of the somewhat similar, although less sensitive, *p*-nitrophenol has been found by Holleman (*Rec.*

trav. chim., 1902, **21**, 432) to vary between 6·1 and 7·3 × 10^{-8}, while Hantzsch gives 9·6 × 10^{-8}. We have tested the constants over all available dilutions. In Table I the first dissociation constants are represented by K_e in order to distinguish them from the colorimetric constants—first, ${}_1K_c$; second, ${}_2K_c$, and third, ${}_3K_c$. The compounds have been arranged in each group as far as possible in the order of diminishing first dissociation constants, K_e. Some of these, however, can be regarded as practically identical, in view of the probable errors mentioned above. The mononitrodihydric, like the mononitromonohydric, phenols are about equal in strength, but the dinitro-compounds, like the dinitrophenols, show a considerable difference in this respect. It is, however, in the relation between K_e and the K_c values that both mono- and di-nitro-dihydric phenols show the greatest individuality: so much so that a single conductivity measurement, combined with a colorimetric determination in a solution of known p_H would serve to distinguish each compound quite clearly.

In Table I, the constants of the nitrophenols are given for comparison, the values of K_e being due to Holleman (*loc. cit.*) and those of K_c to Michaelis and Gyemant (*Biochem. Z.*, 1920, **109**, 166). The fourth, fifth, and sixth columns give the constants of the tautomeric changes into the yellow, then the red, and purple forms (if any). The figures in the third column assign each compound to its predominant tautomeric form (Ph. = phenolic; Qu. = quinonoid) and attempt to define its strength as an acid dissociating in this form (K_e').

The experimental constants summarise the equilibria between the tautomeric forms, HM_1 and HM_2, and the products of their dissociation. In the equations, HM_1 stands for the phenolic acid (Ph.), $HO{\cdot}R{\cdot}NO_2$, and HM_2 for the quinonoid or *aci*-form (Qu.), $O{:}R{:}NO{\cdot}OH$:

$$K_e = \frac{[H^{\cdot}][M'_1 + M'_2]}{[HM_1 + HM_2]} \quad \text{and} \quad K_c = \frac{[H^{\cdot}][HM_2 + M'_2]}{[HM_1 + M'_1]} \; *$$

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* K_e and K_c are the " apparent " constants, due to the two forms present together, and obtained by electrometric and colorimetric measurements, respectively. Experimental results show that these measurements do in many cases give " mass-action " or Ostwald constants, which do not vary more than those obtained in the case of some of those acids having no tautomeric forms. The expressions for K_e and K_c do not, however, imply constancy unless there are other constants regulating the equilibria between the tautomeric forms, as has been shown by Noyes (*J. Amer. Chem. Soc.*, 1910, **32**, 815; see also Prideaux, " Theory and Use of Indicators," p. 129, Constable, 1917). The drift in the case of some constants may be due to the fact that the equilibria between the tautomeric forms do not obey the law of " mass " or concentration action. We have not yet been able to devise a method of testing this hypothesis.

TABLE I.

Compound.	K_e, as p_K.	K_e', as p_K.	${}_1K_c$, as p_K.	${}_2K_e$, as p_K.	${}_3K_c$ as p_K.
Mononitrophenols.					
2-Nitrophenol	7·17	7·04 (Qu.)	6·05		
4- ,, ...	7·19		7·2		
3- ,, ...	8·0		8·35		
Dinitrophenols.					
2 : 6-Dinitrophenol	3·57		3·70		
2 : 4- ,, ...	4·0		4·06		
2 : 3- ,, ...	4·89				
2 : 5- ,, ...	5·16		5·16		
3 : 4- ,, ...	5·37				
3 : 5- ,, ...	6·68				
Dihydric mononitrophenols.					
3-Nitropyrocatechol	5·73	5·55 (Qu.)	4·95	11·03	High
2-Nitroresorcinol	5·80	5·80 (Qu.)	Low	6·34	—
4- ,, ...	5·98	5·98 (Ph.)	8·81	—	—
2-Nitroquinol	6·00	6·00 (Qu.)	3·25	7·2	10·2
4-Nitropyrocatechol	6·45	6·30 (Qu.)	5·56	10·96	—
Dihydric dinitrophenols.					
2 : 4-Dinitroresorcinol	3·05	3·3 (Ph.)*	3·9 ± 0·4	—	—
3 : 5-Dinitropyrocatechol	3·54	3·14 (Qu.)	3·25	10·3	High
4 : 6-Dinitroresorcinol	3·98	4·60 (Ph.)	4·22	—	—
2 : 6-Dinitroquinol	4·00 ± 0·2	3·3 (Qu.)†	2·8	5·2	9·05

* $a = 0·4 \quad 0·5 \quad 0·7 \qquad p_{K_e}' = 3·21 \quad 3·24 \quad 3·47.$

† $a = 0·177 \quad 0·211 \quad 0·236 \quad 0·280 \qquad p_{K_e}' = 2·96 \quad 3·13 \quad 3·43 \quad 3·64.$

Thus the constant K_c measures the tendency of the compound to undergo the tautomeric change under the influence of diminishing hydrogen-ion concentration, whether this change takes place in the undissociated molecule or in the ion. The constant K_e contains the molecules and ions which take part in the dissociation of the first hydrogen ion from both the tautomeric forms. Although neither of the two true dissociation constants can be deduced from K_e by a rigid algebraic proof, yet by taking into account numerical relations, on the assumption that the colorimetric constant gives correctly the relative amount of coloured form, $HM_2 + M'_2$, the true dissociation constants of HM_1 or HM_2 may be obtained. The following is an outline of the reasoning and calculations by which these true constants (column 3 in Table I) were derived.

Where K_e is much greater than K_c, it is practically identical with the true dissociation constant of the phenolic acid. On the other hand, where K_e is much less than K_c, it is practically identical with the true constant of the quinonoid acid. Where $K_e = K_c$, the original Ostwald theory of indicators must be used, since ionisation proceeds *pari passu* with tautomeric change. Where K_e and K_c are of the same order, but not too close to one another, the true constants may be calculated as described below. The limiting ratios of K_e to K_c at which such calculations become necessary will depend on the accuracy with which the original constants are defined by the experimental work.

If $K_e \gtreqless 100K_c$, K_e is the constant of the phenolic acid, for even at a degree of ionisation $\alpha = 0{\cdot}8$, the amount of the coloured tautomeride is negligible. In the case of the mononitro-compounds, the degree of ionisation does not exceed 0·05 at the highest dilutions investigated. In the case of the dinitro-compounds, we have not, in determining the constants, taken into account degrees of ionisation exceeding 0·5, since, according to the usual estimate, the secondary ionisation of a dibasic acid may begin to be appreciable at this degree of primary ionisation.

Even at much lower ratios of K_e/K_c, the true constant of the phenolic acid, K'_e, is not far from the observed constant, K_e. The correction of K_e to K'_e will be greatest if all the quinonoid tautomeride is present as ion, and we will make this assumption. The total ion concentration is $M'_1 + M'_2$ and this is equal to $M'_1 + x$, if x is the degree of transformation (of total compound) into M'_2. Suppose that the ratio K_e/K_c is 20, and that the conductivity is determined at a degree of dissociation of 0·25; then

$$(1 - x)/x = [\mathrm{H}^{\cdot}]/K_c \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which x is the degree of colour change, and

$$(1 - \alpha)/\alpha = [\mathrm{H}^{\cdot}]/K_e \quad . \quad . \quad . \quad . \quad . \quad (2)$$

in which α is the degree of ionisation.

Therefore, on the above assumption,

$$[\mathrm{H}^{\cdot}] = K_e(1 - \alpha)/\alpha = 3K_e \text{ and } x = 1/[1 + 3K_e/K_c) = 1/61$$

Also $$3(M'_1 + 1/61) = (1 - M'_1 - 1/61),$$

therefore $M'_1 = 0{\cdot}233$, and the true constant of HM_1, $K'_e = 0{\cdot}233[\mathrm{H}^{\cdot}]/0{\cdot}75$

or $$K_e' = 0{\cdot}93K_e; \text{ since } K_e = 0{\cdot}25[\mathrm{H}^{\cdot}]/0{\cdot}75.$$

Correction of the Constant of the Phenolic Acids.—When the ratio K_e/K_c is still lower, the observed constant may be corrected for the presence of the ion of the quinonoid form. From the conductivity results we select one or more values of α. Then $p_{\mathrm{H}} = p_{K_e} + \log \alpha/(1 - \alpha)$. By introducing the corresponding value of $[\mathrm{H}^{\cdot}]$ into the equation $\log (1 - x)/x = p_{K_c} - p_{\mathrm{H}}$, the value of x is obtained.

Now since $x = M'_2$, $M'_1 = \alpha - x$, and $HM_1 = 1 - \alpha$,

therefore $$p_{K'_e} = p_{\mathrm{H}} - \log (\alpha - x) + \log (1 - \alpha) \quad . \quad . \quad (3)$$

Correction of the Constants of the Quinonoid Acids.—If K_c is greater than K_e, the observed electrolytic dissociation is mainly that of the quinonoid form. The most natural assumption, and that which requires the largest correction of the observed constants, is that all the ion consists of M'_2, the remainder of the quinonoid form being present as HM_2. The true constant K'_e of this form can be determined by a simple calculation. Selecting a degree of transformation x (*e.g.*, 0·8), we calculate the corresponding value of $[H^\cdot]$ from equation (1) above. Then substitute this in equation (2), and calculate α and hence also $x - \alpha$ from the equation $\log (1 - \alpha)/\alpha = p_{K_e} - p_H$.

Thus in the case of 3-nitropyrocatechol, when $x = 0{\cdot}8$, $p_H = 5{\cdot}55$, $\alpha = 0{\cdot}402$ at this p_H, and $x - \alpha = 0{\cdot}398$. Hence

$$p_{K'_e} = p_H + \log (x - \alpha)/\alpha = 5{\cdot}54 \quad . \quad . \quad . \quad (4)$$

In calculating α from equation (2) in cases where K_e shows a trend, that value of p_{K_e} is used which corresponds according to the conductivity results to *each* value of α. In these cases, the corrected constant also shows a trend.

Orientation and Polarity.—The orientation of the compounds tabulated can be regarded as exerting influence upon (1) the strengths of the phenolic acids, (2) the strengths of the quinonoid acids, and (3) the colorimetric constants of the tautomeric changes. The two principal aspects of orientation which have received most attention are (*a*) the propinquity of substituting groups, the well-known effects of which have long been systematised without any hypothesis as to mechanism; and (*b*) the alternation of substituting groups, the effect of which is intelligible on the electronic theory of valency.

It should be possible to explain the order of the constants which represent (1), (2), and (3) in a quantitative manner, by the principles (*a*) and (*b*). The residual charges, detected by Lewis's method in the electronic formulæ for $\cdot NO_2$ (Lowry, *Trans. Faraday Soc.*, 1923, **18**, 285), cause it to act as a key radical in maintaining the polarity of a conjugated system. The nitrogen atom, on account of its mixed bond in $\cdot NO_2$ ($O{=}N \dashrightarrow O$), assumes a virtual positive charge and confers a virtual negative charge on the carbon atom to which it is attached, and this by alternation of the mean directions in which the electrons oscillate or vibrate, strengthens the virtual negative charges on the carbons in the 3- and 5-positions and weakens those in the 2-, 4-, and 6-positions.

Thus when a hydroxyl group is attached to the 3- or 5-position, weaker phenolic acids should result than when it is attached to the 2-, 4-, or 6-position. There might also be a reciprocal effect of the hydroxyl group on the nitro-group, which will become evident when the $\cdot OH$ becomes $\dot{\colon}O$. Our results seem to show that the effect of

·NO·OH on :O, and reciprocally, is similar to that of $\cdot NO_2$ on ·OH; so that factors (*a*) and (*b*) act in the same sense on the quinonoid as on the phenolic acids. These effects may first be illustrated by the nitro- and dinitro-phenols.

o-Nitrophenol, in which factors (*a*) and (*b*) are both at a maximum, has a slightly higher constant than *p*-nitrophenol, in which (*b*) is favourable but (*a*) is less so (Holleman, *loc. cit.*). Both are higher in Table I than *m*-nitrophenol, in which (*b*) is unfavourable. The greater tendency to tautomeric change in the *o*- and *p*-compounds is shown by the dissociation of the ortho-compound largely as a quinonoid substance, and of the meta-compound in the phenolic direction. In the case of *p*-nitrophenol, dissociation and tautomeric change are almost parallel.

In the case of the dinitrophenols also, it is remarkable how close the colorimetric lies to the dissociation constant in those cases where both are known. The order of the constants agrees on the whole with the alternate polarity theory. In the strongest, 2 : 6-dinitrophenol, (*a*) and (*b*) are at a maximum; in the 2 : 4-compound (*b*) is favourable and (*a*) not so favourable. In 2 : 3-dinitrophenol, the strengthening effect of the 2-nitro-group is somewhat weakened by the opposing effect of the 3-nitro-group. In the 2 : 5-compound, the opposing effect of the second nitro-group is more marked as the hydroxyl group is exposed to it more directly. In the 3 : 4-, the nitro-group opposing the dissociation is nearer to the hydroxyl than that which favours it. In the 3 : 5-, both nitro-groups alternate incorrectly. It must be noted that the "opposition" of a nitro-group which alternates incorrectly is really only a smaller enhancing effect, since all dinitro-phenols are stronger acids than mononitro-phenols, owing, no doubt, to the more numerous chances for the formation of the quinonoid molecule *whatever* the position of the second nitro-group.

In contrast to the nitrophenols, the nitro-dihydric phenols show the most varied relations between first dissociation and colorimetric constants.

The Mononitro-compounds.—K_c is greater than K_e in the case of 2-nitroquinol, 2-nitroresorcinol, 3- and 4-nitropyrocatechols, 3 : 5-dinitropyrocatechol, and 2 : 6-dinitroquinol, which therefore dissociate chiefly or wholly as quinonoid acids; whilst K_e is greater than K_c in the case of 4-nitro-, and 2 : 4- and 4 : 6-dinitroresorcinol, which therefore dissociate chiefly or wholly as phenolic acids.

The first dissociation constants of the mononitro-compounds are of the order 1×10^{-6}, the constant thus being increased about 10-fold by the introduction of a second hydroxyl group into the molecule of *o*-nitrophenol. The nitro-group is in the ortho-position to at least one hydroxyl group, *i.e.*, condition (*a*) is favourable, in all the compounds except 4-nitropyrocatechol, which has a distinctly lower constant than the others. One might perhaps expect 3-nitropyrocatechol to be a weaker acid than the 4-nitro-isomeride, instead of *vice versa.* The position of the second hydroxyl group appears, however, to have only a slight effect on the constant. Regarding the first four compounds in this series as derivatives of *o*-nitrophenol, we see that the effect of the second hydroxyl group in decreasing the constant $p_K = 7{\cdot}17$ (*i.e.*, increasing the constant K_c) of *o*-nitrophenol increases in the order 4 = 5, 3, 6. The order of increasingly favourable alternating effect (which agrees with the increase of constant in the order, *o*-, *m*-, and *p*-, in the case of mononitrophenols and some other compounds) is 4, 6, 5, 3. The order of increase in the case of the dihydroxybenzoic acids (with one hydroxyl group ortho to the carboxyl group) is 5, 4, 6, 3 (Lehfeldt, "Electrochemistry," Longmans), which is identical with the order required by condition (*a*) above, *i.e.*, mere propinquity without alternation. The dissociation of the carboxyl group would appear to be more powerfully affected by propinquity, (*a*), and that of the ·NO·OH group by alternation, (*b*), where the two principles are in opposition.

The Dinitro-compounds.—It was considered surprising by Bader (*loc. cit.*), in view of the negative character of hydroxyl, that dinitroquinol should be a weaker acid than 2 : 6-dinitrophenol. This may perhaps be explained as being due to a diminution of the negative polarity of the carbon attached to the ·NO·OH group by the opposing positive polarity of the carbon attached to the 4-hydroxyl group. 2 : 4-Dinitroresorcinol, in which the alternate polarities are in tune, is a stronger acid than 2 : 4- or even than 2 : 6-dinitrophenol.

Comparing the constants of the dinitro- with those of the corresponding mononitro-compounds, there is seen to be an increase in K (decrease in p_K of 1·5—3 units). The polarity of the second nitro-group always enhances that of the first, since the list examined includes only *m*-dinitro-compounds.

The order of the corrected constants is the same as that of the mononitro-compounds from which they are derived :

3-Nitropyrocatechol > 2-nitroresorcinol > 2-nitroquinol = 4-nitroresorcinol *
3 : 5-Dinitropyrocatechol > 2 : 4-dinitroresorcinol = 2 : 6-dinitroquinol > 4 : 6-dinitroresorcinol

* The meta-dinitro-derivative of 4-nitropyrocatechol has not been examined.

The tendency to undergo tautomeric change is measured by the colorimetric constants. The order of these is different from that of the dissociation constants, and is nearly the same in the dinitro-compounds as in the mononitro-compounds from which they are derived. Thus it is apparently the orientation of one nitro-group in relation to the two hydroxyl groups which determines the number of tautomeric changes and the p_H at which they occur.

Order of ${}_1K_c$.

* 2-Nitroresorcinol > 2-nitroquinol > 3-nitropyrocatechol > 4-nitropyrocatechol > 4-nitroresorcinol,
2 : 6-Dinitroquinol > 3 : 5-dinitropyrocatechol > 2 : 4-dinitroresorcinol > 4 : 6-dinitroresorcinol †

* The constant is too high to be measured.
† The constant is rather uncertain.

To the second and third colorimetric constants given in our previous communication have now been added all those which can be determined. The nitroresorcinols do not give second constants, with the single exception of the 2-isomeride which undergoes its first change of colour at an exceptionally low p_H, whilst the change of the 4-isomeride occurs at an exceptionally high p_H. The second changes (half-way) to the red or brown forms occur at p_H's from 4 to 6 units lower than the changes (half-way) to the yellow form. The order of the second constants is very similar to that of the first:

${}_1K_c$ | 2-N.R. > 2 : 6-N.Q. > 2-N.Q. = 3 : 5-N.C. > 2 : 4-N.R. > 3-N.C. > 4-N.C. > 4-N.R.
${}_2K_c$ | 2 : 6-N.Q. > 2-N.R. > 2-N.Q. > 3 : 5-N.C. > 3-N.C. = 4N.C.

The only compounds which undergo the third change, to purple, are nitroquinols and nitropyrocatechols (but not 4-nitropyrocatechol); those in the latter class, however, only show this change in such strong alkali that p_{K_3} could not be determined. The order of the third constants is nearly the same as that of the second:

${}_2K_c$ | 2 : 6-N.Q. > 2-N.Q. > 3 : 5-N.C. > 3-N.C. = 4-N.C.
${}_3K_c$ | 2 : 6-N.Q. > 2-N.Q. > 3 : 5-N.C. > 3-N.C. —

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