The Dissociation Constants of Some Disubstituted Anilines and Phenols in Aqueous Solution at 25 °C

R. A. Robinson

Institute for Materials Research, National Bureau of Standards, Washington, D.C. 20234

The dissociation constants of six disubstituted anilines and of five disubstituted phenols in aqueous solution at 25 °C have been measured using the spectrophotometric method. Consideration is given to the extent to which these dissociation constants can be predicted from corresponding values for monosubstituted anilines and phenols. In addition, the question as to whether the pK value of a substituted aniline can be predicted from the pK value of a phenol with substituents in the same positions is also investigated.

Key Words: Dissociation constant, substituted anilines, substituted phenols.

1. Introduction

In an earlier paper [1][1] the results of measurements of the pK values of the six dichloroanilines and the six dichlorophenols in aqueous solution at 25 °C have been reported. The conclusions drawn from this work can be summarized briefly in two statements. In the first place, the pK value of any one of ten dichlorosubstituted compounds (2,6-dichloroaniline and 2,6-dichlorophenol being exceptions) could be predicted knowing the pK values of the monosubstituted chlorocompounds. This utilizes an additivity rule which can be illustrated as follows; the pK value of phenol itself is 9.998, that of m-chlorophenol is 9.130 and that of p-chlorophenol is 9.418 [2]. Thus, m-Cl substitution lowers the pK value of phenol by 0.868 and p-Cl substitution by 0.580. If the substituent effects were strictly additive, 3,4-dichloro substitution should lower the value of pK by 1.448 and the pK value of 3,4-dichlorophenol should be 8.550. The observed value is 8.585, differing from the calculated by only 0.035. The additivity rule predicts pK values with an accuracy which varies from 2,4-dichloroaniline ($pK_{obs} = 2.02$, $pK_{calc} = 2.03$) to 2,3-dichloroaniline ($pK_{obs} = 1.76$, $pK_{calc} = 1.92$). Only in the case of 2,6-dichloroaniline and 2,6-dichlorophenol did the additivity rule fail to predict the observed value within these limits, the difference between observed and calculated pK values being 0.28 in the case of 2,6-dichloroaniline and 0.27 in the case of 2,6-dichlorophenol. In these two instances we have compounds with three substituent groups in adjacent positions, Cl, NH_2 (or

OH), Cl, and it is not surprising that there should be steric effects which interfere with the additivity relation.

Secondly, it was found that a linear relationship existed between the pK value of a dichloroaniline, pK_A, and the pK value of the corresponding dichlorophenol, pK_P. This could be expressed by the equation

$$pK_A = -9.047 + 1.401\, pK_P.$$

For example, it was found that pK_P was 6.791 for 2,6-dichlorophenol, whence this equation gives $pK_A = 0.467$. The experimental value is 0.422. It should be noted that this relationship holds for 2,6-disubstituted compounds, although the additivity rule, mentioned above, fails in this instance.

These conclusions are valid for a particular class of disubstituted anilines and phenols, the dichloro compounds. It is of interest, however, to inquire whether they have application to a wider group of disubstituted anilines and phenols. For this reason, measurements have now been made on a group of disubstituted compounds in which the substituent groups are $-Br$, $-Cl$, $-CH_3$, and $-NO_2$.

2. Experimental Procedure

2.1. Materials

4-Chloro-2-methylaniline hydrochloride was recrystallized twice from 80 percent ethanol, Cl found 19.92 percent, calc 19.91 percent, ϵ_2 2,510 at 291 mμ in alkaline solution. 2,4-Dibromoaniline was recrystallized first from heptane and then from a mixture of

---

[1] Figures in brackets indicate the literature references at the end of this paper.

heptane and petroleum ether, mp 80 °C, ϵ_2 2,160 at 300 mμ in alkaline solution, ϵ_1 280 at 273 mμ and 200 at 280 mμ in acid solution. 2,6-Dibromoaniline was recrystallized twice from heptane, mp 83.5 °C, ϵ_2 2,550 at 294 mμ, ϵ_1 350 at 272 mμ and 370 at 279 mμ. 2-Methyl-5-nitroaniline was recrystallized once from benzene, mp 108 °C, ϵ_2 2,060 at 355 mμ. 4-Methyl-2-nitroaniline was recrystallized once from benzene, mp 117.5 °C, ϵ_2 4,230 at 427 mμ. 4-Methyl-3-nitroaniline was recrystallized twice from benzene, mp 79.5 °C, ϵ_2 1,580 at 357 mμ. 4-Chloro-2-methylphenol was recrystallized three times from petroleum ether, mp 47.5–48 °C ϵ_2 3,030 at 300 mμ, ϵ_1 1,680 at 281 mμ, and isosbestic points ϵ 1,010 at 271 mμ and 1,600 at 284 mμ. 2,4-Dibromophenol was recrystallized three times from heptane, mp 36 °C, ϵ_2 3,700 at 309 mμ, ϵ_1 2,090 at 286 mμ, ϵ 1,280 at 274 mμ and 1,970 at 291 mμ. 2,6-Dibromophenol was recrystallized twice from petroleum ether, mp 56 °C, ϵ_2 5,250 at 304 mμ, ϵ_1 2,170 at 276 mμ and 2,170 at 284 mμ, ϵ 1,130 at 269 mμ and 2,160 at 284 mμ. 2-Methyl-4-nitrophenol was recrystallized twice from water, mp 96 °C, ϵ_2 13,310 at 414 mμ, ϵ_1 6,340 at 327 mμ, ϵ 3,510 at 358 mμ. 4-Methyl-3-nitrophenol was recrystallized from benzene and then from a mixture of heptane and petroleum ether, mp 77.5–78 °C, ϵ_2 1,410 at 390 mμ, ϵ_1 2,050 at 340 mμ, ϵ 1,340 at 369 mμ.

2.2. Outline of Method

The principle of the spectrophotometric determination of a pK value is as follows. Consider three solutions of a phenol, all at the same stoichiometric concentration. Let there be added to one enough acid to convert the phenol entirely into the molecular form, HN. To the second let there be added sufficient alkali to convert the phenol entirely into its ionized form, N⁻. Let the third contain a buffer solution in which the phenol is present partly in its molecular form and partly in its ionized form. Let α be the degree of dissociation of the phenol. Then if D_1, D_2, and D, respectively, are the optical densities of these three solutions, measured at the same wavelength in cells of the same length, it follows that

$$\alpha = (D - D_1)/(D_2 - D_1) \text{ and}$$
$$\alpha/(1-\alpha) = (D - D_1)/(D_2 - D). \quad (1)$$

This dissociation constant for the process

$$HN \rightleftharpoons H^+ + N^-$$

is

$$K = \frac{a_{H^+} \cdot m_{N^-}}{m_{HN}} \frac{\gamma_{N^-}}{\gamma_{HN}} = a_{H^+} \cdot \frac{\alpha}{1-\alpha} \frac{\gamma_{N^-}}{\gamma_{HN}} \quad (2)$$

which can be written as

$$pK = p(a_H\gamma_{Cl}) - \log \alpha/(1-\alpha) - \log \gamma_{N^-}/(\gamma_{HN}\gamma_{Cl}^-) \quad (3)$$

where $p(a_H\gamma_{Cl})$ is a characteristic of the buffer solution employed and γ designates an activity coefficient.

Accurate values of the pK are obtained if $\alpha \approx 0.5$, which means that pK should be approximately equal to $p(a_H\gamma_{Cl})$. Thus, the measurement of the pK value of a phenol is best performed with a buffer solution which satisfies this condition. The buffer solutions used in this work were (1) an equimolal mixture of potassium dihydrogen phosphate and disodium hydrogen phosphate, $p(a_H\gamma_{Cl}) \approx 7.0$; (2) a mixture of tris(hydroxymethyl)aminomethane (m) and its hydrochloride (0.9845m), $p(a_H\gamma_{Cl}) \approx 8.3$; (3) a mixture of borax (m) and sodium chloride (1.855m), $p(a_H\gamma_{Cl}) \approx 9.2$. The $p(a_H\gamma_{Cl})$ values of the buffer solutions depend on the concentrations of the buffer constituents; the requisite values have been tabulated by Bates and Gary [3]. These $p(a_H\gamma_{Cl})$ values are altered to a small extent by the phenol in the buffer solution whose dissociation into hydrogen ions increases the acidity of the buffer solution slightly. The correction to the $p(a_H\gamma_{Cl})$ values has already been considered [4].

It would be expected that the last term in eq (3) would be either small or negligible; in the former case an extrapolation can be made to give the true value of pK at infinite dilution. For the phenols studied in this work, the value of pK proved to be independent of the buffer concentration, indicating that the last term of eq (3) was negligible and, therefore, the best value of pK was assumed to be the average of those found at different concentrations of the buffer solution.

The dissociation of the anilinium ion or a substituted anilinium ion can be represented as

$$BH^+ \rightleftharpoons H^+ + B$$
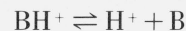
with a dissociation constant

$$K = \frac{m_{H^+} \cdot \alpha}{1-\alpha} \frac{\gamma_{H^+} \cdot \gamma_B}{\gamma_{BH^+}} \quad (4)$$

or

$$pK = -\log m_{H^+} - \log \alpha/(1-\alpha)$$
$$- \log (\gamma_{H^+} \cdot \gamma_B)/\gamma_{BH^+}. \quad (5)$$

The pK values of most substituted anilines are less than 3 and it is therefore preferable to make measurements in solutions of a strong acid of known concentration. In this work, hydrochloric acid was used. Then, if m_{HCl} is the stoichiometric concentration of hydrochloric acid added to the aniline solution and m is the stoichiometric concentration of aniline, m_{H^+} in eq (5) can be equated to $m_{HCl} - m(1-\alpha)$. Again it is desirable to use hydrochloric acid solutions of concentration such that $\alpha \approx 0.5$. If dilute solutions of hydrochloric acid are used, the last term of eq (5) should be negligible and this proved to be the case. But if pK was small, so that moderately concentrated solutions of hydrochloric acid had to be used, as in the case of 2,6-dibromoaniline and 4-methyl-2-nitro-

214

aniline, this term could no longer be neglected and the true value of pK had to be obtained by extrapolation of $[-\log m_{H^+} - \log \alpha/(1-\alpha)]$ to zero acid concentration; this procedure has already been used for 2,6-dichloroaniline [1] and for o-nitroaniline [2].

In one instance, 4-chloro-2-methylaniline, with a pK value ≈ 3.8, it was necessary to use a succinic acid-sodium hydrogen succinate buffer solution. The equation for the dissociation constant now becomes

$$pK = p(a_H\gamma_{Cl}) - \log \alpha/(1-\alpha) + \log (\gamma_{BH^+} \cdot \gamma_{Cl^-})/\gamma_B. \quad (6)$$

Values of $p(a_H\gamma_{Cl})$ for this buffer solution have been tabulated [3] and the activity coefficient term can be written

$$\log (\gamma_{BH^+} \cdot \gamma_{Cl^-})/\gamma_B = -2AI^{1/2}/(1+1.5I^{1/2}) \quad (7)$$

where A is the parameter of the Debye-Hückel equation (0.5108 kg$^{-1/2}$ mole$^{1/2}$ at 25 °C).

3. Results and Discussion

3.1. Additivity Effects

The detailed experimental results are given in tables 1–11 and summarized in table 12. The pK value for 4-methyl-2-nitrophenol is taken from a previous publication [5]. Table 12 also contains values of pK calculated on the assumption that the effect of double substitution in an aniline or phenol can be compounded as the sum of the separate monosubstitution effects. Thus the pK value of phenol itself, 9.99_8, [2] is raised to 10.28_7 in o-cresol, [6] the substitution effect of the o-methyl group being -0.28_9; the pK value of p-chlorophenol is 9.41_8 [2] so that the substitution effect of the p-chloro group is 0.58_0. If these effects are strictly additive, the combined effects of o-methyl and p-chloro substitution should be 0.29_1 giving $pK = 9.70_7$ for 4-chloro-2-methylphenol, which agrees very well with the observed value of 9.70_6. Substituent effects were calculated from the pK values of o-nitrophenol [7], m-nitrophenol [8], and m-nitroaniline [10]; for other groups the data of Biggs [6] or of Biggs and Robinson [2] were used.

Inspection of table 12 shows that the additivity rule holds with varying degrees of success. It is remarkably good with 4-chloro-2-methylphenol and 4-methyl-3-nitrophenol and not so good with 4-methyl-2-nitrophenol. It is possible that the additivity rule fails when bulky ortho substituted groups are present because these can produce steric inhibition of resonance. Thus the rule fails badly with 2,6-dibromoaniline and 2,6-dibromophenol as it does with the corresponding dichloro compounds [1] and with 2,6-dinitrophenol [10]. Perhaps the most remarkable failure of additivity is found with 4-methyl-2-nitroaniline; the additivity rule holds for the corresponding phenol with only moderate success.

TABLE 1. *Dissociation constant of 4-chloro-2-methylaniline*

Aniline concentration 2.27×10^{-4} M, cell length 1 cm, wavelength 291 mμ, D_1 0, D_2 0.569

I	m	$p(a_H\gamma_{Cl})$	D	$\log\frac{D-D_1}{D_2-D}$	$2\log\gamma$	pK	pK(corr)
0.02017	0.02	3.898	0.257	-0.084	-0.117	3.865	3.853
.03018	.03	3.892	.251	$-.103$	$-.140$	3.855	3.848
.04019	.04	3.887	.245	$-.121$	$-.157$	3.851	3.848
.05019	.05	3.884	.239	$-.140$	$-.171$	3.853	3.851
.06020	.06	3.882	.236	$-.150$	$-.183$	3.849	3.847
.08021	.08	3.878	.229	$-.172$	$-.203$	3.847	3.846
.10021	.10	3.875	.223	$-.191$	$-.219$	3.847	3.846

The buffer solution was a mixture of sodium hydrogen succinate (m) and hydrochloric acid ($0.6667m$) equivalent to a mixture of sodium hydrogen succinate ($0.3333m$), succinic acid ($0.6667m$), and sodium chloride ($0.6667m$).

TABLE 2. *Dissociation constant of 2,4-dibromoaniline*

Aniline concentration 9.31×10^{-5} M, cell length 4 cm, wavelength 300 mμ, D_1 0.009, D_2 0.804

$m_{HCl} \times 10^3$	D	$\log\frac{D-D_1}{D_2-D}$	$-\log m_{H^+}$	pK
5.846	0.568	0.375	2.235	1.860
6.852	.535	.291	2.166	1.875
9.591	.474	.149	2.020	1.871
13.80	.408	.003	1.862	1.859
16.28	.370	$-.080$	1.790	1.870
16.39	.375	$-.069$	1.787	1.856
21.02	.322	$-.188$	1.679	1.867
29.59	.257	$-.344$	1.530	1.874

TABLE 3. *Dissociation constant of 2,6-dibromoaniline*

Aniline concentration 4.92×10^{-5} M, cell length 4 cm, wavelength 294 mμ, D_1 0, D_2 0.502

m_{HCl}	D	$\log\frac{D-D_1}{D_2-D}$	$\log m_{H^+}$	pK'	pK'(calc)
0.1021	0.436	0.817	-0.991	0.174	0.182
.2042	.382	.499	$-.690$	.191	.195
.3063	.337	.306	$-.514$	.208	.209
.4084	.300	.167	$-.389$	.222	.222
.5105	.271	.065	$-.292$	.227	.236
.6126	.242	$-.037$	$-.213$	.250	.249
.7147	.218	$-.121$	$-.146$	.267	.263
.8168	.196	$-.200$	$-.088$	.288	.277
.9189	.183	$-.248$	$-.037$	.285	.290
1.021	.165	$-.318$	.009	.309	.304

pK'(calc) $= 0.168 + 0.133$ m_{HCl}.

TABLE 4. *Dissociation constant of 2-methyl-5-nitroaniline*

Aniline concentration $5.05 \times 10^{-4}M$ cell length 1 cm, wavelength 355 mμ, D_1 0.105, D_2 1.042

$m_{HCl} \times 10^3$	D	$\log\frac{D-D_1}{D_2-D}$	$-\log m_{H^+}$	pK
2.004	0.772	0.393	2.731	2.338
4.007	.613	.074	2.424	2.350
6.011	.522	$-.096$	2.242	2.338
8.014	.451	$-.232$	2.114	2.346
10.02	.403	$-.331$	2.014	2.345
14.03	.336	$-.485$	1.865	2.350

TABLE 5. *Dissociation constant of 4-methyl-2-nitroaniline*

Aniline concentration 1.752×10^{-4} M, cell length 1 cm, wavelength 427 mμ, D_1 0, D_2 0.740

m_{HCl}	D	$\log \dfrac{D-D_1}{D_2-D}$	$-\log m_{H^+}$	pK'	pK'(calc)
0.1037	0.581	0.563	0.984	0.421	0.422
.2075	.471	.243	.683	.440	.442
.3112	.390	.047	.507	.460	.461
.4150	.326	−.104	.382	.486	.480
.5187	.280	−.216	.285	.501	.499
.6224	.243	−.311	.206	.517	.519
.7262	.210	−.402	.139	.541	.538
.8299	.185	−.477	.081	.558	.557
.9337	.163	−.549	.030	.579	.577
1.037	.146	−.609	−.016	.593	.596

pK'(calc) $= 0.403 + 0.186\, m_{HCl}$.

TABLE 6. *Dissociation constant of 4-methyl-3-nitroaniline*

Aniline concentration 3.49×10^{-4} M, cell length 1 cm, wavelength 357 mμ, D_1 0.088, D_2 0.551

$m_{HCl} \times 10^3$	D	$\log \dfrac{D-D_1}{D_2-D}$	$-\log m_{H^+}$	pK
1.002	0.336	+0.062	3.076	3.014
1.503	.284	−.134	2.885	3.019
2.004	.250	−.269	2.750	3.019
2.505	.225	−.377	2.646	3.023
3.006	.207	−.461	2.561	3.022
3.507	.193	−.533	2.490	3.027
4.008	.181	−.600	2.428	3.028
5.010	.165	−.700	2.326	3.026

TABLE 7. *Dissociation constant of 4-chloro-2-methylphenol*

Phenol concentration 3.25×10^{-4} M, cell length 1 cm, wavelength 300 mμ, D_1 0.012, D_2 0.984

I	$p(a_H\gamma_{Cl})$	D	$\log \dfrac{D-D_1}{D_2-D}$	pK	pK(corr)
0.010	9.234	0.254	−0.480	9.714	9.702
.015	9.237	.257	−.472	9.709	9.701
.020	9.237	.258	−.470	9.707	9.701
.025	9.238	.257	−.472	9.710	9.705
.030	9.239	.256	−.475	9.714	9.710
.035	9.239	.256	−.475	9.714	9.711
.040	9.239	.256	−.475	9.714	9.711

The buffer solution was a mixture of borax (m) and sodium chloride ($1.855m$), $I = 3.855m$.

TABLE 8. *Dissociation constant of 2,4-dibromophenol*

Phenol concentration 1.76×10^{-4} M, cell length 1 cm, wavelength 309 mμ, D_1 0.007, D_2 0.652

I	$p(a_H\gamma_{Cl})$	D	$\log \dfrac{D-D_1}{D_2-D}$	pK	pK(corr)
0.01	8.176	0.461	0.376	7.800	7.790
.02	8.207	.471	.409	7.798	7.793
.03	8.232	.480	.439	7.793	7.790
.04	8.251	.486	.460	7.791	7.789
.05	8.266	.491	.478	7.788	7.786
.06	8.280	.495	.492	7.788	7.786
.07	8.292	.499	.507	7.785	7.784
.08	8.302	.499	.507	7.795	7.794
.09	8.312	.502	.518	7.794	7.793
.10	8.321	.505	.530	7.791	7.790

The buffer solution was a mixture of tris(hydroxymethyl)amino methane (m) and its hydrochloride ($0.9845m$), $I = 0.9845m$.

TABLE 9. *Dissociation constant of 2,6-dibromophenol*

Phenol concentration 3.05×10^{-5} M, cell length 4 cm, wavelength 300 mμ, D_1 0.008, D_2 0.641

I	$p(a_H\gamma_{Cl})$	D	$\log \dfrac{D-D_1}{D_2-D}$	pK	pK(corr)
0.01	7.111	0.467	0.421	6.690	6.684
.02	7.080	.463	.408	6.672	6.669
.03	7.058	.456	.384	6.674	6.672
.04	7.040	.452	.371	6.669	6.667
.05	7.026	.443	.342	6.684	6.683
.06	7.013	.444	.345	6.668	6.667
.08	6.992	.433	.310	6.682	6.681
.10	6.974	.432	.307	6.667	6.666

The buffer solution was an equimolal mixture of potassium dihydrogen phosphate (m) and disodium hydrogen phosphate (m), $I = 4m$.

TABLE 10. *Dissociation constant of 2-methyl-5-nitrophenol*

Phenol concentration 4.04×10^{-4} M, cell length 1 cm, wavelength 430 mμ, D_1 0.005, D_2 0.685

I	$p(a_H\gamma_{Cl})$	D	$\log \dfrac{D-D_1}{D_2-D}$	pK	pK(corr)
0.01	8.176	0.190	0.427	8.603	8.593
.02	8.207	.202	.390	8.597	8.592
.03	8.232	.209	.368	8.600	8.597
.04	8.251	.217	.344	8.595	8.593
.05	8.266	.223	.326	8.592	8.590
.06	8.280	.226	.317	8.597	8.595
.07	8.292	.232	.300	8.592	8.591
.08	8.302	.237	.286	8.588	8.587
.09	8.312	.239	.280	8.592	8.591
.10	8.321	.244	.266	8.587	8.586

The buffer solutions were mixtures of tris(hydroxymethyl)amino methane (m) and its hydrochloride ($0.9845m$), $I = 0.9845m$.

TABLE 11. *Dissociation constant of 4-methyl-3-nitrophenol*

Phenol concentration 4.69×10^{-4} M, cell length 1 cm

I	$p(a_H\gamma_{Cl})$	D	$\log \dfrac{D-D_1}{D_2-D}$	pK	pK(corr)
			Wavelength 390 mμ, D_1 0.232, D_2 0.660		
0.02	8.207	0.352	-0.409	8.616	8.611
.04	8.251	.360	$-.370$	8.621	8.619
.05	8.266	.362	$-.360$	8.626	8.624
.06	8.280	.362	$-.360$	8.640	8.638
.08	8.302	.371	$-.318$	8.620	8.619
.10	8.321	.377	$-.290$	8.611	8.610
			Wavelength 430 mμ, D_1 0.010, D_2 0.493		
0.02	8.207	0.146	-0.407	8.614	8.609
.04	8.251	.152	$-.381$	8.632	8.630
.05	8.266	.157	$-.359$	8.625	8.623
.06	8.280	.157	$-.359$	8.639	8.637
.08	8.302	.165	$-.326$	8.628	8.627
.10	8.321	.172	$-.297$	8.618	8.617

The buffer solutions were mixtures of tris(hydroxymethyl)amino methane (m) and its hydrochloride $(0.9845m)$, $I = 0.9845m$.

TABLE 12. pK *values of substituted anilines and phenols in aqueous solution at 25 °C*

	pK(Aniline)			pK(Phenol)		
	Obsd.	Calcd.	Diff.	Obsd.	Calcd.	Diff.
4-Chloro-2-methyl	3.848	3.822	0.026	9.706	9.707	-0.001
2,4-Dibromo	1.867	1.794	.073	7.790	7.805	$-.015$
2,6-Dibromo	0.168	0.463	$-.295$	6.674	6.888	$-.214$
2-Methyl-5-nitro	2.345	2.306	.039	8.592	8.644	$-.052$
4-Methyl-2-nitro	0.403	0.210	.193	7.597	7.494	.103
4-Methyl-3-nitro	3.022	2.933	.089	8.622	8.619	.003

3.2. A Linear Relation Between the pK Values of Substituted Anilines and Those of Substituted Phenols

Figure 1 is a plot of the pK values of 25 substituted anilines (pK_A) against the pK value of the corresponding substituted phenol (pK_P). It is clear that, with six exceptions, the experimental values lie close to a straight line. The exceptions are o-methyl, p-methoxy, o-nitro, 4-chloro-2-methyl, 2-methyl-5-nitro, and 4-methyl-2-nitroaniline and phenol. The best straight line through the remaining 19 points in figure 1, determined by the method of least squares, is given by the equation:

$$pK_A = a\, pK_P - b, \qquad (8)$$

with $a = 1.293$ and $b = 8.254$. This equation is essentially an expression of the Hammett Rule [11]. It enables the pK value of a substituted aniline to be predicted from the pK value of the corresponding phenol (or vice versa) with an average difference between observed and calculated values of 0.07_7, the smallest difference being found in the case of p-nitro substitution (0.00_1) and the greatest in the case of
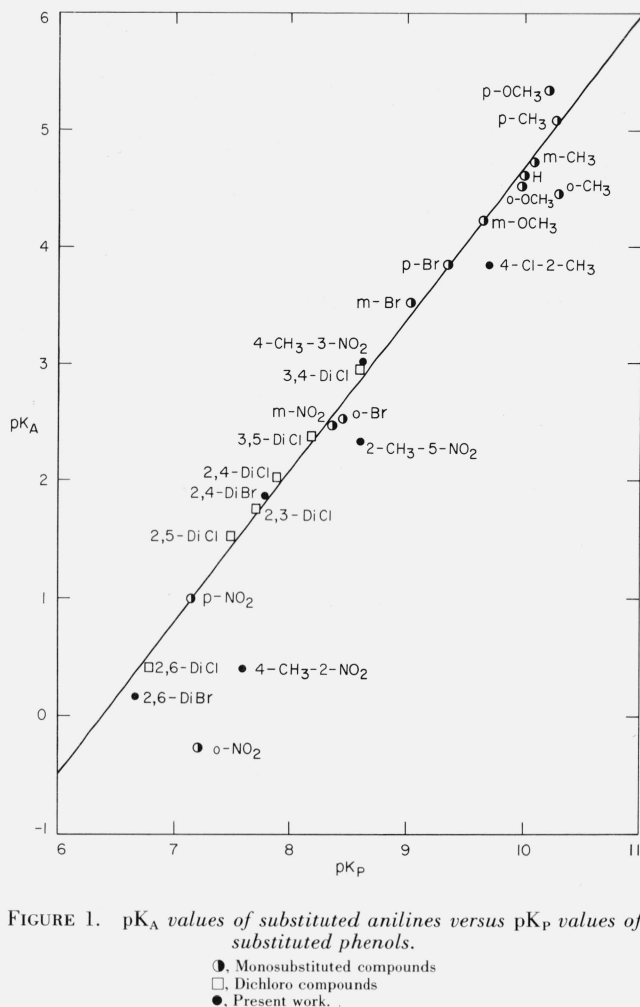

FIGURE 1. pK_A *values of substituted anilines versus* pK_P *values of substituted phenols.*

◓, Monosubstituted compounds
□, Dichloro compounds
●, Present work.

2,6-dibromo substitution (0.20_6). In a previous publication [1], a similar linear relationship was discussed but two linear equations were proposed, one for the monosubstituted anilines and phenols and another for dichloroanilines and dichlorophenols. Naturally, the use of four parameters leads to better agreement with the experimental data; a two-parameter equation is used here because it is not so much agreement with the experimental data that is of interest but the exceptional cases which are widely divergent. The exceptions among the monosubstituted anilines and phenols are o-methyl, p-methoxy, and o-nitro compounds for which deviations from the straight line of figure 1 of 0.59_8, -0.39_8, and 1.35_9, respectively, are found, a positive sign being used if the observed pK_A value of a substituted aniline is greater than that calculated using eq (8). Three exceptions are found among the disubstituted anilines and phenols, the 4-chloro-2-methyl, 2-methyl-5-nitro, and 4-methyl-2-nitroanilines and phenols. The discrepancies amount to 0.44_8, 0.51_0, and 1.16_6, respectively. It will be noted that there is o-methyl substitution in two instances and o-nitro substitution in the third. Both substituents lead to anomalies in the monosubstituted

248–733 O–67—3

compounds. Moreover, the anomaly is about the same in both monosubstituted and disubstituted compounds. Thus it is 0.59_8 for *o*-methyl monosubstitution and 0.44_8 or 0.51_0 if there is an *o*-methyl radical in a disubstituted compound; it is 1.35_9 for *o*-nitro monosubstitution and 1.16_6 if there is an *o*-nitro group in a disubstituted compound. This suggests that anomalies in monosubstituted compounds carry over more or less unchanged on further substitution by a "well-behaved" radical. On the average, the anomaly is 0.51_9 for *o*-methyl substitution and 1.26_2 for *o*-nitro-substitution; eq (8) can, therefore, be extended by retaining the value of $a = 1.293$ but reducing b to -9.516 for *o*-nitro substitution and b to -8.773 for *o*-methyl substitution. The agreement between observed pK_A values and those calculated with the aid of these b values in eq (8) is now -0.09_5 for *o*-nitro monosubstitution and -0.07_9 for *o*-methyl monosubstitution; in the case of disubstituted compounds, the discrepancy is 0.09_6 for the 4-methyl-2-nitro compounds, 0.07_1 for the 4-chloro-2-methyl compounds, and 0.00_9 for the 2-methyl-5-nitro compounds.

4. References

[1] R. A. Robinson, J. Res. NBS **68A** (Phys. and Chem.) No. 2, 159 (1964).
[2] A. I. Biggs and R. A. Robinson, J. Chem. Soc. (London) 388 (1961).
[3] R. G. Bates and R. Gary, J. Res. NBS **65A** (Phys. and Chem.) No. 6, 495 (1961).
[4] R. A. Robinson and A. K. Kiang, Trans. Faraday Soc. **51,** 1398 (1955).
[5] R. A. Robinson and R. G. Bates, J. Res. NBS **70A** (Phys. and Chem.) No. 6, 553 (1966).
[6] A. I. Biggs, Trans. Faraday Soc. **52,** 35 (1956).
[7] R. A. Robinson and A. Peiperl, J. Phys. Chem. **67,** 1723 (1963).
[8] R. A. Robinson and A. Peiperl, J. Phys. Chem. **67,** 2860 (1963).
[9] E. E. Sager, R. A. Robinson, and R. G. Bates, J. Res. NBS **68A** (Phys. and Chem.) No. 3, 305 (1964).
[10] R. A. Robinson, M. M. Davis, M. Paabo, and V. E. Bower, J. Res. NBS **64A** (Phys. and Chem.) No. 4, 347 (1960).
[11] L. P. Hammett, Physical organic chemistry, ch. VII (McGraw-Hill Book Co., Inc., New York, N.Y., 1940).