

Ionization Constants of Four Dinitrophenols in Water at 25 °C

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Thermodynamic ionization constants of 2,3-, 2,5-, 3,4-, and 3,5-dinitrophenols in aqueous solution at 25° C have been determined by a spectrophotometric method. The respective values found, expressed as pK , are 4.95₉, 5.21₀, 5.42₂, and 6.69₂. pK has also been determined potentiometrically for 2,3- and 3,5-dinitrophenols; the respective values obtained are 4.98 and 6.66. The experimental pK values for all six dinitrophenols are lower than the calculated values based on pK data for phenol and the mononitrophenols.

Spectral absorption curves are presented for the ionized and unionized forms of the four dinitrophenols.

1. Introduction

“Concentration” ionization constants of the six dinitrophenols were determined by Holleman and Wilhelmy [1],² and thermodynamic ionization constants have since been determined for all but the 2, 3- and 3,5-isomers. Only the 2,4- and 2,6-isomers are readily obtained commercially at the present time. The remaining isomers were synthesized in this laboratory for a study of the comparative acidic behavior of the six dinitrophenols in benzene.³ The same materials were used for the work reported in this paper; namely, the determination of thermodynamic pK values for the 2,3- and 3,5-isomers and redetermination of thermodynamic pK values for the 2,5- and 3,4-isomers.

2. Experimental Procedure

2.1. Materials

3,5-Dinitrophenol was made by converting 1,3,5-trinitrobenzene to 3,5-dinitroanisole [1, 2] and then demethylating [3]. The product was recrystallized from water as the dihydrate; this was dehydrated overnight in a vacuum oven, then recrystallized from benzene-cyclohexane and dried at 90° for one hour (mp, 124.3 to 125.0° C).

2,3-, 2,5-, and 3,4-Dinitrophenols were prepared simultaneously by nitrating *m*-nitrophenol and then were separated by fractional crystallizations [1, 4]. Finally, each compound was recrystallized twice from the solvent indicated: 2,3-Dinitrophenol (from water), mp 146.5 to 147.0° C; 2,5-dinitrophenol (from 95% ethanol), mp 105.8 to 106.2° C; 3,4-dinitrophenol (from benzene), mp 135.1 to 135.5° C.

Potentiometric weight titrations for 2,3-dinitrophenol and for 3,5-dinitrophenol indicated a purity of not less than 99.8 percent.

2.2. Determination of pK values

The *spectrophotometric procedure* followed in determining the pK values was devised by Robinson and coworkers [5] in a research program one objective of which is to test the applicability of Hammett's equation [6] to substituted phenols.

The pK of the dinitrophenol was calculated from the equation

$$pK = pH - \log[(D - D_1)/(D_2 - D)] - \log \gamma_R - \Delta pH. \quad (1)$$

The spectrophotometric data (see second term on right side of eq (1)) were obtained at 25.0 ± 0.1° C with a Beckman Model DU quartz spectrophotometer, using optical absorption cells 1 cm in length. The symbols D_1 , D_2 , and D signify the spectral absorbances (optical densities) of solutions containing the same total molar concentration of dinitrophenol present as unionized molecules, phenolate ions, or mixtures of the two, respectively. In measuring the limiting spectral absorbances, the dinitrophenol was dissolved in aqueous hydrochloric acid of $pH \approx 2$ (for D_1 values) or in aqueous sodium hydroxide of $pH \approx 12$ (for D_2 values). Measurements of D were made for at least three differently buffered solutions having known pH values which were close to the expected pK value of the dinitrophenol. The absorbances were measured at two or three wavelengths. Phosphate buffer mixtures [7] were used in determining the pK of 3,5-dinitrophenol, and succinate buffer mixtures [8] were used for the remaining dinitrophenols. The compositions and pH values of buffers used are given in tables 2 and 3.

The following modification of Davies' equation [9] was used to calculate γ_R , the activity coefficient of the phenolate ion:⁴

$$-\log \gamma_R = A \sqrt{I} / (1 + \sqrt{I}) - 0.2 I. \quad (2)$$

The final term in eq (1), ΔpH , is a correction applied because the addition of the phenol to the buffer mixtures causes some changes in the pH of

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² Figures in brackets indicate the literature references at the end of this paper.

³ M. M. Davis and M. Paabo, work in progress.

⁴ The modification consists of substituting 0.2 I for 0.1 I [5]. I symbolizes the ionic strength. The value for the parameter A in the Debye-Hückel-Onsager equation has been recomputed because a more accurate value for the dielectric constant of water is available. The value of A adopted earlier [10] was 0.509; the new value is 0.5115 [11].

the solution, a change which becomes more important as the buffer becomes more dilute [12]. This correction can be put in the form

$$\Delta pH \approx 0.4343[m_3/(m_1+m_2)] (K/K_R) \times [(K_R+h)^2/(K+h)h], \quad (3)$$

where m_1 and m_2 are the molalities of the buffer salts, m_3 is that of the phenol, h is the hydrogen ion concentration, K_R is the ionization constant of the acid of the buffer, and K is the ionization constant of the phenol.

In the *potentiometric determination of pK* for 2,3- and 3,5-dinitrophenols, a 100-ml portion of 0.01-M aqueous solution of each compound was titrated at $25^\circ \pm 1^\circ$ C with 0.1-M sodium hydroxide. The potential was measured between glass and saturated calomel electrodes [13].

Values of pK were computed from the equation

$$pK = pH - \log \left\{ \frac{([B^-] + [H^+])}{([HB] - [H^+])} \right\} + \{ (0.5115\sqrt{I}) / (1 + 1.5\sqrt{I}) \}. \quad (4)$$

The pK value obtained for 2,3-dinitrophenol was 4.98 ± 0.005 , and the pK value for 3,5-dinitrophenol was 6.66 ± 0.001 .

3. Results and Discussion

Molar absorption curves for the dinitrophenols in aqueous acid and alkali are presented in figures 1 to 3. Optical constants are summarized in table 1.

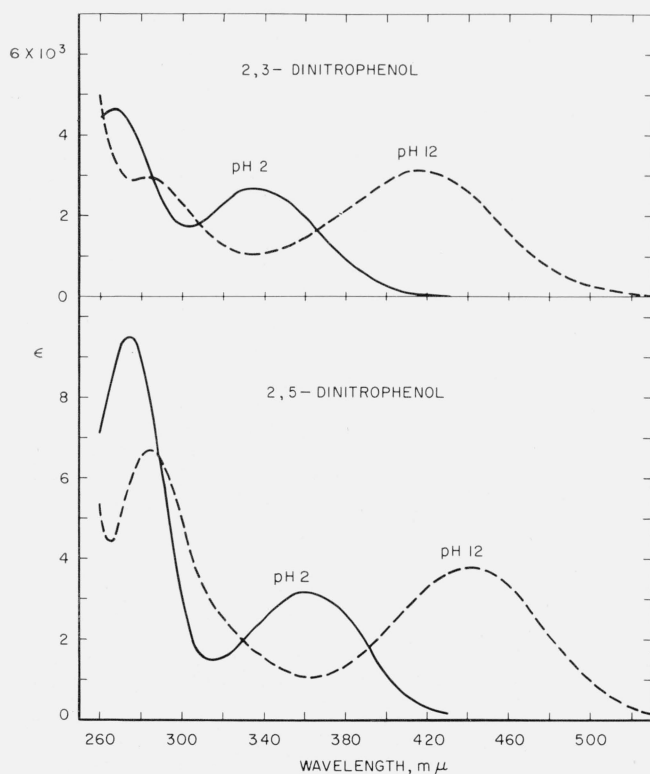


FIGURE 1. Absorption spectra of 2,3-dinitrophenol and 2,5-dinitrophenol in aqueous acid ($pH \approx 2$) and alkali ($pH \approx 12$).

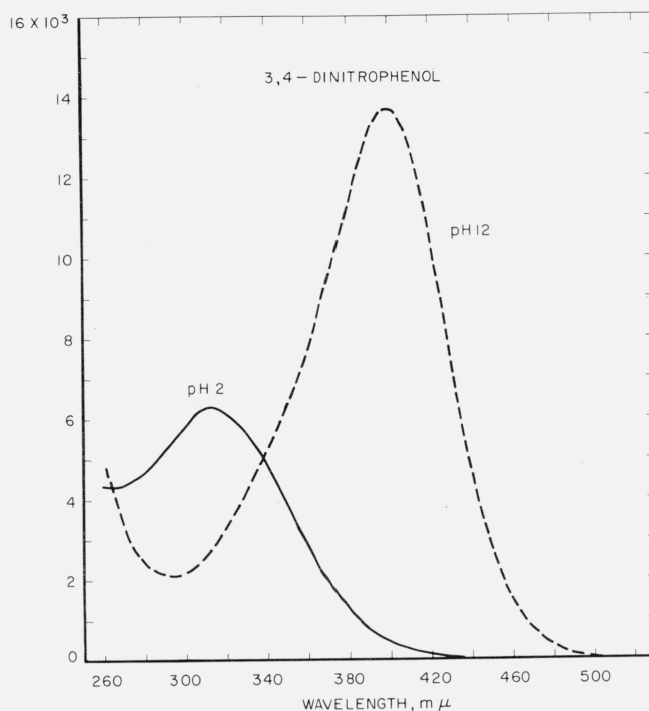


FIGURE 2. Absorption spectra of 3,4-dinitrophenol in aqueous acid ($pH \approx 2$) and alkali ($pH \approx 12$).

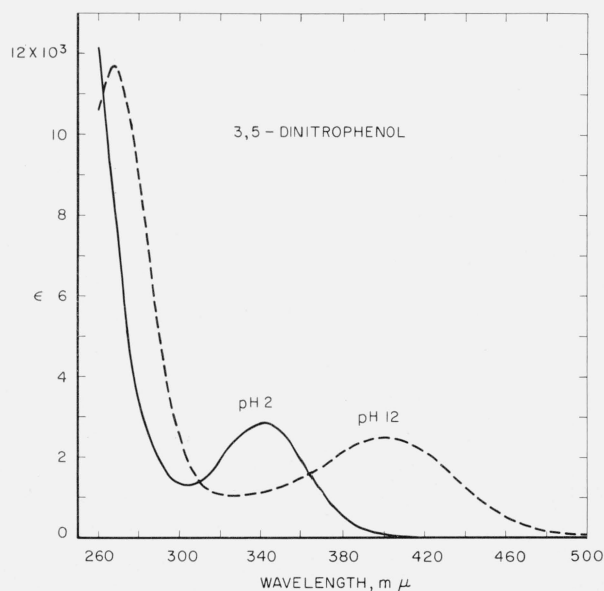


FIGURE 3. Absorption spectra of 3,5-dinitrophenol in aqueous acid ($pH \approx 2$) and alkali ($pH \approx 12$).

TABLE 1. Optical constants of dinitrophenols in aqueous acid and alkali

Compound	Absorption bands				Isosbestic points	
	pH=2		pH=12			
	λ_{\max} m μ	ϵ_{\max}	λ_{\max} m μ	ϵ_{\max}	$\lambda_{\text{m}\mu}$	ϵ
2,3-Dinitrophenol.....	$\left\{ \begin{array}{l} 265 \\ 335 \end{array} \right.$	$\left\{ \begin{array}{l} 4620 \\ 2700 \end{array} \right.$	$\left\{ \begin{array}{l} 282 \\ 416 \end{array} \right.$	$\left\{ \begin{array}{l} 2930 \\ \text{a } 3130 \end{array} \right.$	$\left\{ \begin{array}{l} 261 \\ 285 \\ 308 \\ 366 \end{array} \right.$	$\left\{ \begin{array}{l} 4500 \\ 2950 \\ 1800 \\ 1700 \end{array} \right.$
2,5-Dinitrophenol.....	$\left\{ \begin{array}{l} 275 \\ 360 \end{array} \right.$	$\left\{ \begin{array}{l} 9500 \\ 3150 \end{array} \right.$	$\left\{ \begin{array}{l} 285 \\ 440 \end{array} \right.$	$\left\{ \begin{array}{l} 6700 \\ \text{a } 3770 \end{array} \right.$	$\left\{ \begin{array}{l} 288 \\ 330 \\ 392 \end{array} \right.$	$\left\{ \begin{array}{l} 6550 \\ 2000 \\ 1800 \end{array} \right.$
3,4-Dinitrophenol.....	$\left\{ \begin{array}{l} 315 \end{array} \right.$	$\left\{ \begin{array}{l} 6300 \end{array} \right.$	$\left\{ \begin{array}{l} 400 \end{array} \right.$	$\left\{ \begin{array}{l} \text{a } 13700 \end{array} \right.$	$\left\{ \begin{array}{l} 264 \\ 338 \end{array} \right.$	$\left\{ \begin{array}{l} 4300 \\ 5000 \end{array} \right.$
3,5-Dinitrophenol.....	$\left\{ \begin{array}{l} 343 \end{array} \right.$	$\left\{ \begin{array}{l} 2900 \end{array} \right.$	$\left\{ \begin{array}{l} 268 \\ 400 \end{array} \right.$	$\left\{ \begin{array}{l} 11700 \\ \text{a } 2480 \end{array} \right.$	$\left\{ \begin{array}{l} 262 \\ 310 \\ 364 \end{array} \right.$	$\left\{ \begin{array}{l} 11000 \\ 1490 \\ 1600 \end{array} \right.$

^a G. Kortüm, Z. physik. Chem. **B42**, 39 (1939), reported values in good agreement with these results in the cases of 2,3-dinitrophenol (3160) and 3,5-dinitrophenol (2450), but not in the cases of 2,5-dinitrophenol (4170) or 3,4-dinitrophenol (5250). (See table on p. 64 of ref. cited.)

Data and results for the ionization constants by the spectrophotometric procedure are summarized in tables 2 and 3.

TABLE 2. Ionization constant of 3,5-dinitrophenol in water at 25° C

Ionic strength ^a	pH	$-\log$ γ_{K-}	D ^b	$\log \frac{D-D_1}{D_2-D}$	pK	pK (corr.)
$\lambda=400 \text{ m}\mu \quad D_1=0.037, D_2=1.341$						
0.2.....	6.772	0.118	0.830	0.191	6.699	6.693
.1.....	6.860	.103	.879	.260	6.703	6.691
.08.....	6.886	.097	.886	.271	6.712	6.696
.04.....	6.959	.077	.917	.318	6.718	6.686
.02.....	7.018	.059	.924	.328	6.749	6.687
$\lambda=410 \text{ m}\mu \quad D_1=0.017, D_2=1.298$						
0.2.....	6.772	0.118	0.793	0.187	6.704	6.698
.1.....	6.860	.103	.839	.252	6.711	6.699
.08.....	6.886	.097	.851	.271	6.712	6.696
.04.....	6.959	.077	.883	.321	6.716	6.684
.02.....	7.018	.059	.889	.329	6.748	6.686
Avg.....						6.692 $K=2.03 \times 10^{-7}$

^a The molar concentration of 3,5-dinitrophenol was 5.4×10^{-4} . The buffer solutions contained equimolar KH_2PO_4 and Na_2HPO_4 .

^b The optical absorption cells were 1 cm in length. D_1 and D_2 symbolize, respectively, the spectral absorbance (optical density) of the unionized phenol and the phenol anion, and D , that of a solution containing a mixture of the two.

TABLE 3. Ionization constants of 2,3-, 2,5-, and 3,4-dinitrophenols in water at 25° C ^a

Buffer mixture No. ^b	2,3-Dinitrophenol 2.17×10 ⁻⁴ M				2,5-Dinitrophenol 1.13×10 ⁻⁴ M				3,4-Dinitrophenol 6.8×10 ⁻⁵ M			
	D	log $\frac{D-D_1}{D_2-D}$	pK	pK (corr.)	D	log $\frac{D-D_1}{D_2-D}$	pK	pK (corr.)	D	log $\frac{D-D_1}{D_2-D}$	pK	pK (corr.)
1----- 2----- 3-----	λ=410 mμ D ₁ =0.019, D ₂ =0.671				λ=430 mμ D ₁ =0.010, D ₂ =0.414				λ=400 mμ D ₁ =0.023, D ₂ =0.930			
	0. 513 . 524 . 534	0. 496 . 535 . 576	4. 965 4. 971 4. 976	4. 962 4. 966 4. 963	0. 270 . 276 . 286	0. 260 . 287 . 335	5. 201 5. 218 5. 216	5. 200 5. 215 5. 209	0. 495 . 519 . 548	0. 035 . 082 . 138	5. 426 5. 424 5. 413	5. 425 5. 422 5. 409
	λ=420 mμ D ₁ =0.009, D ₂ =0.676				λ=440 mμ D ₁ =0.005, D ₂ =0.426				λ=410 mμ D ₁ =0.011, D ₂ =0.866			
	0. 517 . 527 . 536	0. 504 . 540 . 577	4. 957 4. 966 4. 974	4. 954 4. 961 4. 961	0. 275 . 284 . 291	0. 252 . 291 . 326	5. 209 5. 215 5. 225	5. 208 5. 212 5. 218	0. 456 . 474 . 500	0. 035 . 072 . 126	5. 426 5. 434 5. 425	5. 425 5. 432 5. 421
1----- 2----- 3-----	λ=430 mμ D ₁ =0.005, D ₂ =0.632				Avg-----5. 21 ₀ K=6. 17×10 ⁻⁶				Avg-----5. 42 ₂ K=3. 78×10 ⁻⁶			
	0. 483 . 493 . 501	0. 506 . 546 . 580	4. 955 4. 960 4. 971	4. 952 4. 955 4. 958								
	Avg-----4. 95 ₉ K=1. 10×10 ⁻⁵											

^a Optical absorption cells 1 cm in length were used throughout. D_1 and D_2 signify, respectively, the spectral absorbance (optical density) of the unionized phenol and the phenol anion, and D symbolizes the absorbance of a solution containing both unionized and ionized phenol.

^b Buffer mixtures Nos. 1, 2, and 3 were mixtures of x -molar sodium hydrogen succinate and x -molar disodium succinate, where $x=0.05, 0.025$, and 0.01 , respectively. The pH values of these buffer mixtures were 5.343, 5.403, and 5.474, respectively.

In table 4, the pK values obtained in this work by the spectrophotometric method are compared with earlier experimental values. pK values for 2,4- and 2,6-dinitrophenols are included in table 4.

TABLE 4. pK values of dinitrophenols in water at 25° C

Dinitrophenol	pK , calc ^a	pK , experimental				ΔpK ^e
		This work	Earlier work ^b			
2,3- -----	5.61	*4.96	4.89 ^d	4.09 ^e	*4.11 ^f	-0.65
2,4- -----	4.36		4.00 ^d	5.22 ^g		-0.25
2,5- -----	5.61	*5.21	5.15 ^d	5.42 ^g		-0.40
2,6- -----	4.42		3.57 ^d	*3.71 ^{h, i}		-0.71
3,4- -----	5.55	*5.42	5.37 ^d	5.42 ^g		-0.13
3,5- -----	6.80	*6.69	6.68 ^d			-0.11

^a Based on the following pK values: Phenol, 9.998; *o*-nitrophenol, 7.210; *m*-nitrophenol, 8.399; *p*-nitrophenol, 7.149. See R. A. Robinson and A. I. Biggs, *Trans. Faraday Soc.* **51**, 901 (1955); A. I. Biggs, *Trans. Faraday Soc.* **52**, 35 (1956).

^b pK values determined at other temperatures are in general harmony with the values cited in this table. For example, L. Michaelis and A. Gyemant, *Biochem. Z.* **109**, 165 (1920); L. Michaelis and R. Krüger, *Biochem. Z.* **119**, 307 (1921); R. Riccardi and P. Franzosini, *Boll. sci. fac. chim. ind., Bologna* **15**, 25 (1957).

^c $\Delta pK = pK_{\text{exptl.}} - pK_{\text{calc.}}$

^d A. F. Holleman and G. Wilhelmy, *Rec. trav. chim.* **21**, 432 (1902). (R. Bader, *Z. physik. Chem.* **6**, 289 (1890), determined ionization constants for all of the dinitrophenols except 3,5-dinitrophenol, but only very approximately.)

^e H. von Halban and G. Kortüm, *Z. physik. Chem.* **A170**, 351 (1934); see also W. D. Bale and C. B. Monk, *Trans. Faraday Soc.* **53**, 450 (1957).

^f R. G. Bates and G. Schwarzenbach, *Helv. chim. acta* **37**, 1069 (1954).

^g C. M. Judson and M. Kilpatrick, *J. Am. Chem. Soc.* **71**, 3110 (1949).

^h G. Kortüm and H. Wilski, *Z. physik. Chem.* **2**, 256 (1954); earlier unpublished work of M. Kortüm-Seiler yielding the same result by a different method is cited.

ⁱ J. F. J. Dippy, S. R. C. Hughes, and J. W. Laxton, *J. Chem. Soc. (London)* **1956**, 2995.

It is evident that the thermodynamic ionization constants, expressed in pK units, agree well in general magnitude with the corresponding "concentration" ionization constants [1], but the thermodynamic values are from 0.01 to 0.14 pK unit higher. Our pK values for the 2,5- and 3,4-isomers are in excellent agreement with the results of Judson and Kilpatrick (table 4, footnote g).

Values of pK for all six dinitrophenols can be calculated from pK data for phenol itself and for the mono-substituted nitrophenols, using the assumption of additivity (see table 4). The experimental pK values are all lower than the calculated values, in agreement with an analogous conclusion of Holleman and Wilhelmy [1]. The disagreement is particularly marked in the case of dinitrophenols substituted in the 2-position.

4. References

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