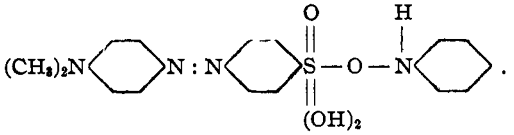
soluble in 50% aqueous pyridine (625 g.). In water, structure[1] (II) is involved; in pyridine, structure (III) is involved; and in 50% pyridine, a hydrated form of (III) probably is involved. Indirect evidences for assuming such hydrated form are at hand—pyridine becomes warm on adding water and a pyridine hydrate[2] has been described. The pyridine salt of helianthine containing one molecule of water probably has the structure

(V).



In other words, the differences in solubility of helianthine in water, pyridine and mixtures of the same can be explained on the basis of involving different forms of the solute such as (II), (III) and (V).

SEATTLE, WASH.

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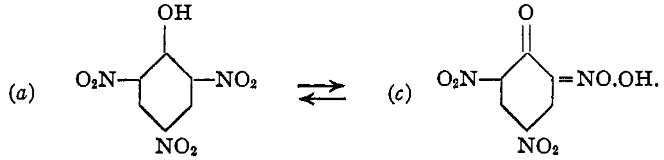
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WASHINGTON.]

# COLORIMETRIC STUDIES OF PICRATE SOLUTIONS.

BY WILLIAM M. DEHN AND ALICE A. BALL.

Received February 27, 1917.

In a recent colorimetric study of chromate solutions by one of us, it was stated[3] that preliminary experiments with picrates in different solvents and under varied conditions of concentration, temperature and alkalinity, in accordance with the conclusion of Hantzsch,[4] indicated equilibria of two isomeric forms of the acid.



Recognition of tautomeric forms of picric acid has been made by various investigators,[5] but perhaps the greatest credit for such recognition should be given to Hantzsch, who in voluminous contributions to the quinones, nitro phenols and the pseudo-acids, has steadfastly maintained[6] a theory

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[1] See preceding paper on methyl orange.

[2] Goldschmidt and Constam, *Ber.*, 16, 2977 (1883). Also see paper following.

[3] THIS JOURNAL, 36, 846 (1914).

[4] *Ber.*, 39, 1077 (1906); 40, 350 (1907). For iso-picric acids see Nietzki and Dietschy, *Ibid.*, 34, 57 (1901).

[5] Draeper, *J. Chem. Soc.*, 99, 2096 (1911)..

[6] *Ber.*, 12, 1803, 1807, 2071 (1879); 32, 575 (1899); 39, 1073, 1084, 3074 (1906); 40, 338, 1533, 1556, 4875 (1907). Compare also Kauffmann, *Ibid.*, 39, 1959 (1906); 40, 843, 4547 (1907); Torrey and Heuter, *Ibid.*, 40, 4332 (1907); Kehrmann, *Ibid.*, 32, 927 (1899); 38, 2577 (1905); 40, 1960 (1907).

of tautomerism to explain color changes. The quinoid structure of colored compounds was proposed by early investigators[1] and later met with strong support, especially from Armstrong.[2] Though apparently irreconcilable with some observations and though vigorously attacked by some investigators,[3] the quinoid theory remains the best explanation of color changes. Not only do the data of this contribution accord well with this theory, but recent investigations along various other lines by other investigation, give a heavy preponderance of evidence in support of it, and to account for the color and the other properties of picrate solutions.

First, and of great importance, may be mentioned the fact that two series[4] of salts of picric acid, the one nearly colorless and the other yellow-to-red, have been prepared. Anselmino[5] obtained the two ammonium salts[6] by working, respectively, with cold and hot solutions. Suida[7] prepared two salts each of various organic bases; Pelet-Jolivet and Henry,[8] with $\alpha$-naphthol; Hantzsch,[9] with pentamethylenediamine, and with various ethers of picric acid,[10] etc.[11]

These two varieties of the respective picrates may in themselves be considered sufficient evidence to prove that picric acid exists in the two

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[1] Würster, *Ber.*, **12**, 1803, 2071 (1879); Bernthsen, *Ann.*, **230**, 162 (1885); **251**, 11, 49, 82 (1899); Nietzki, *Chem. organ. Farbenstoffen*, **21–27**, 199 (1906).

[2] *Ber.*, **9**, 950 (1876); *Proc. Chem. Soc.*, **1882**, 27; **1892**, 101, 189, 195; **1893**, 53, 55, 63, 206; **1897**, 228; **1902**, 101; *J. Chem. Soc.*, **87**, 1272 (1905).

[3] See especially Baly's recent contributions in the *J. Chem. Soc.* See also THIS JOURNAL, **37**, 979 (1915); *J. Soc. Chem. Ind.*, **34**, 399 (1915); *J. Soc. Colourist*, **31**, 39; also Hantzsch, *Ber.*, **48**, 1327 (1915).

[4] Yellow and red varieties of thallium picrates have been known for a long time. Descloiseaux and Lamy, *Paris Acad. Sci.*, **1868**. Rabe found their transition temperature to be 46°. *J. physik. Chem.*, **38**, 175 (1901). For mercury salts see Hantzsch and Auld, *Ber.*, **39**, 1105 (1906).

[5] *Ber.*, **41**, 2996 (1908). Hantzsch apparently anticipated Anselmino; *Ibid.*, **40**, 351 (1907). Stepanoff confirms Anselmino's work and gives the conditions of conversion of the one form into the other; *J. Russ. Phys. Chem.*, **42**, 495 (1910). See also Koresynski, *Anz. Kaiser. Akad. Wiss.*, **1908**, 633.

[6] For other metallic picrates see Silberrad and Phillips, *Proc. Chem. Soc.*, **24**, 22; *J. Chem. Soc.*, **93**, 474 (1908). Kast gives a complete bibliography, "Keitsch. ges. Schiesssprengstoffwesen," **6**, 7, 31, 67. Tschugajew and Chlopin, *Z. anorg. Chem.*, **86**, 241 (1914).

[7] *Ber.*, **41**, 1909 (1908).

[8] *Bull. soc. chem.*, [4] **5**, 623 (1909); Sisley, *Ibid.*, [4] **3**, 919 (1908).

[9] *Ber.*, **40**, 351 (1907). . For colored compounds of picric acid and benzaldehyde-phenylhydrazone, see Vecchiotti, *Atti r. Accad. Lincei*, **22**, 103 (1913).

[10] *Ber.*, **39**, 1073, 1084, 3074 (1906); **40**, 338, 1533, 4875 (1907). Torrey and Hinter, *Ibid.*, **40**, 4332 (1907).

[11] Straus and Ackermann, *Ibid.*, **43**, 603 (1910); Tingle and Benke, THIS JOURNAL, **31**, 1318 (1909); Jerusalem, *J. Chem. Soc.*, **95**, 1275 (1908).

differently constituted forms[1] shown above. However, other positive evidences are at hand.

In non-dissociating media Marchwald[2] and Draeper[3] found picric acid to be colorless. Walden[4] found similar results in liquid sulfur dioxide. We have found that picric acid is whitened by contact with oily pyrophosphoric acid. From these observations the conclusion may be drawn that the one form (benzoid) of picric acid is colorless and the other form (quinoid) is yellow-to-red.

That its solutions, as well as its dry salts, may exist as equilibria mixtures of these two varieties is indicated by a large mass of other experimental evidences. Indeed, with the picrates, as with the chromates, many apparently discordant data can be reconciled only on the basis of such tautomeric equilibria.

Three conditions, tending to convert one form into the other, are: (1) concentration, (2) heat, and (3) alkalinity—that is, an increase of any one of these conditions gives at once an increase of the colored isomer.

Adding water to anhydrous solutions of picric acid produces[5] a strong color-intensifying effect. This is especially marked on adding water to alcoholic solutions. The influence of dilution with the same solvent will be shown below and the consequential direct disturbance of the benzoid-quinoid equilibrium will be discussed.

Heating[6] aqueous or alcoholic solutions of picric acid produces easily

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[1] Though recent workers (Buttle and Hewitt, *J. Chem. Soc.*, **95**, 1755 (1909), Draeper, *Ibid.*, **99**, 2094 (1911)) have confirmed a quinoid structure for picric acid, others have advanced objections to the same. Baly and Rice (*J. Chem. Soc.*, **103**, 2094 (1913)) maintain that Hantzsch's *aci*-formula must be eliminated, since picric acid and trinitroanisole, exhibiting similar light-absorption phenomena, must possess similar structural formulas. However, it must be observed that the evidences and conclusions of these authors are not convincing; in fact, an opposite conclusion may be drawn from their very observations. "An interesting fact about picric acid is the readiness with which it gives the yellow form in alcohol solution, compared with trinitroanisole. Whereas the latter gives at first a colorless solution in alcohol, which under the influence of light passes into the yellow form, the former at once gives the yellow form—in alcohol." Certainly the isomerization of both compounds is indicated here (compare Hantzsch, *Ber.*, **39**, 1079 (1906); **48**, 1327 (1915)). While denying the existence of the *aci*-form, Baly and Rice advocate *four* forms for trinitroanisole and picric acid. *J. Chem. Soc.*, **103**, 2095 (1912). Stepanow (*J. Russ. Phys. Chem. Soc.*, **42**, 488, 495) questions the existence of two forms for picric acid and attempts to explain its color phenomena on a crystallographic basis.

[2] *Ber.*, **33**, 1128 (1900).

[3] *J. Chem. Soc.*, **99**, 2094 (1911); *Proc. Chem. Soc.*, **27**, 244.

[4] *Ber.*, **32**, 2864 (1899).

[5] Bortini, *Z. physik. Chem.*, **87**, 104 (1914). Vignon (*Rev. gén. mat. Color*, **13**, 156) gives ratios of the color of 1% solutions in water, alcohol, ether and benzene as 1000 : 256 : 2.4 : 2.1.

[6] Georgievics, *Ber.*, **39**, 1536 (1906); *Monatsh.*, **32**, 319 (1911); Sommerhoft, *Collegium*, **1914**, 225; *Z. Farb. Ind.*, **5**, 270 (1906). Benzene may be used to separate the isomerides of picric acid.

observed darkenings of color. Melting dry picric acid or heating its dry salts produces the same effect. It is evident, therefore, that the formation of the dark-colored form (quinoid) always precedes explosions of picric acid.

The color-intensifying effect[1] of alkalies[2] on solutions of nitrophenols is well known, however, their quantitative influence on picric acid is now studied for the first time, and will be discussed below.

Though much work[3] has been done on the absorption spectra of picric acid, quite varied data and conclusions have been obtained by the different investigators. Buttle and Hewitt[4] found practically no difference in the spectra of acidic and alkaline aqueous solutions of picric acid. Baly and Rice[5] obtained spectra of the acid in various solvents and, while denying the existence of the *aci*-form, unconvincingly[6] postulate *four* forms for the acid. It seems more evident that their curves indicate two forms, one for picric acid in ionizing media and the other in non-ionizing media. Bortini's[5] studies lead to the conclusion that equilibria of the colorless and the colored forms exist in solution. For instance, an absolute alcohol solution contains largely the nitro form; water and 90%

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[1] Light acting on solutions of nitro compounds also disturbs the benzoid-quinoid equilibrium. See Baly and Rice, *J. Chem. Soc.*, **103**, 2094 (1913).

[2] Stepanoff, *J. Russ. Phys. Chem. Soc.*, **42**, 488 (1910); *Ann.*, **373**, 219 (1910), discusses equilibria of Hantzsch's two isomeric forms and the decoloring effect of hydrogen chloride. Perhaps an oxonium form of the salt is to be preferred to the structure given. Hantzsch's, *Ber.*, **39**, 1104 (1906), also shows, by the extinction method, the decoloring effect of hydrogen chloride. Assuming the picric acid of 1 g. in 1000 cc. of water to be 100%, he finds such solution: +10 cc. *N*/100, 97.8%; +10 cc. *N*/10 HCl, 90.6%; +10 cc. *N*/HCl, 68.2%; +30% HCl, 20.2%; 0.1 g. picric acid in 1000 cc. of 30% HCl, 6.7%.

[3] Phipson, *J. Chem. Soc.*, **7**, 424 (1855); Haerlin, *Ann. Physik*, [2] **118**, 70 (1863); Melde, *Ibid.*, **126**, 264 (1864); Kruss, *Ber.*, **15**, 1243 (1882); Knoblauch, *Ann. Physik*, [3] **43**, 728 (1889); Boehlendorff, *Dissertation* (1890); Buss, *Dissertation* (1896); Spring, *Rec. trav. chim.*, **15**, 1 (1897); Buttle and Hewitt, *J. Chem. Soc.*, **95**, 1755 (1909); Baly and Rice, *Ibid.*, **103**, 2094 (1913); *Proc. Chem. Soc.*, **29**, 216; Bortini, *Z. physik. Chem.*, **87**, 104 (1914); Wright, *J. Chem. Soc.*, **103**, 528 (1913); **105**, 669 (1914).

[4] *J. Chem. Soc.*, **95**, 1758 (1909). The authors account for these facts on the basis of complete dissociation of picric acid in the concentrations used.

[5] *Loc. cit.*

[6] It must be observed that some of the solvents used by Baly and Rice partially or completely form salts or molecular compounds with picric acid. For instance, piperidine (Rosenheim and Schidrowitz, *J. Chem. Soc.*, **73**, 143 (1898); dimethylaniline (Jerusalem, *Ibid.*, **95**, 1275 (1909)); benzene (Fritzsche, *Ann.*, **109**, 247 (1859)); Kurilow, *Z. physik. Chem.*, **23**, 676 (1897); Hofmann and Arnoldi, *Ber.*, **39**, 339 (1906); anthracene (Berthelot, *Bull. soc. chim.*, **7**, 34 (1867)); Graebe, *Ann. Supl.*, **7**, 297 (1870); Kremann, *Monatsh.*, **26**, 143 (1905); *Gazz. chim. ital.*, **28**, I, 71 (1898); Sisley, *Bull. soc. chim.*, [9] **3**, 919 (1909). For relations between absorption spectra of acids and their salts, see Wright, *J. Chem. Soc.*, **103**, 528 (1913); **105**, 669 (1914). See Hantzsch's recent criticism of Baly's work, *Ber.*, **48**, 1328 (1915).

alcohol solutions contain largely the *aci*-form. When either form is largely in excess of the other, Beers' law holds; otherwise deviations from Beers' law result but are quite satisfactory accounted for. These observations are also confirmed by our experiments.

Among other physico-chemical studies, undertaken largely to determine the degrees of dissociation of picrate solutions, may be mentioned: (1) electrical conductivities, (2) partitions in immiscible solvents, (3) rates of esterification, (4) rates of decomposition of diazoacetic ester, (5) boiling points.

The conductance data of water,[1] of various alcohols,[2] and of mixtures of the same as solvents invariably showed that the acid is strong but does not follow Ostwald's dilution law. While the variations found cannot be attributed to experimental error,[3] they are quite readily accounted for if one assumes that two forms of the acid are involved—one, the benzoid or nitro form being a weak acid, the other, the quinoid or *aci*-form, being a strong acid.

The behavior of picric acid in immiscible solvents[4] and its deviations from the partition law may be explained on the basis that the acid tends: (1) To form molecular compounds with some of the solvents used, and (2) to form largely the colorless isomer in the immiscible solvent and[3] to form largely the colored isomer in the water.

Studies of the catalytic action of picric acid in esterification[5] experiments have showed that whereas in aqueous solutions both hydrogen chloride and picric acid have very similar effects, in alcohol solutions the latter is much weaker than the former.[6] This is to be expected if picric acid in these two solvents exists in different forms.

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[1] Ostwald, *J. prakt. Chem.*, [2] **32**, 354 (1885); *Z. physik. Chem.*, **1**, 77, 82 (1887); Bader, *Ibid.*, **6**, 300 (1890); Rothmund and Drucker, *Ibid.*, **46**, 845 (1903); Jones and Jacobson, *Am. Chem. J.*, **40**, 355 (1908); Smith and Jones, *Ibid.*, **50**, 33 (1913); Gorke, *Z. physik. Chem.*, **61**, 500 (1908); Kendall, *Proc. Roy. Soc.*, **85A**, 200 (1911). For electrical endosmose, see Elissatoff, *Z. physik. Chem.*, **79**, 405 (1912).

[2] Shall, *Ibid.*, **14**, 701 (1894); Millar, *Ibid.*, **85**, 129 (1913); Brauve, *Ibid.*, **85**, 170 (1913); Goldschmidt, *Z. electrochem.*, **15**, 4 (1909); Goldschmidt and Thuesen, *Z. physik. Chem.*, **81**, 30 (1913).

[3] Compare Rothmund and Drucker, *Z. physik. Chem.*, **46**, 827 (1908), and Gorke, *Ibid.*, **61**, 500 (1908).

[4] Rothmund and Drucker, *Z. physik. Chem.*, **46**, 851 (1903); Herz and Fisher, *Ber.*, **37**, 4748 (1904); **38**, 1142 (1905); Herz and Kurzer, *Z. Electrochem.*, **16**, 871 (1910); Hendrixson, *Z. anorg. Chem.*, **13**, 73; Herz and Lewy, *Z. Electrochem.*, **11**, 820 (1905); Sisley, *Bull. soc. chim.*, [3] **27**, 901 (1902).

[5] Goldschmidt, *Ber.*, **28**, 3218 (1895); **29**, 2208 (1896); Goldschmidt and Sunde, *Ibid.*, **39**, 711 (1906); Goldschmidt and Udby, *Z. physik. Chem.*, **60**, 720 (1907); Goldschmidt, *Z. Electrochem.*, **15**, 4 (1909); Goldschmidt, *Z. physik. Chem.*, **70**, 627 (1910); Goldschmidt, *Z. Electrochem.*, **17**, 604 (1911); Goldschmidt and Thuesen, *Z. Electrochem.*, **81**, 30 (1913).

[6] *Ber.*, **39**, 719.

Studies of the catalytic action of picric acid in the process of decomposition of diazoacetic ether[1] have also showed varied results in different absolute alcohols and the same containing traces and larger quantities of water.

Cryoscopical and ebullioscopical studies[2] also have showed certain abnormalities.

In general all the deviations and abnormalities quoted can quite satisfactorily be accounted for on the benzenoid-quinoid bases given above.

## Method of Colorimeter Study.

As with the chromates and methyl orange,[3] so with the picrates, solutions were put up in square uniform bottles of clear glass and 39 mm. cross-section. Solutions were prepared in concentrations from saturation[4] down to 0.00001%, calculated as free picric acid. The respective tenths of the following respective concentrations were prepared: 10, 1.0, 0.1, 0.01, 0.001, 0.0001, 0.00001. When necessary, intermediate concentrations were prepared.

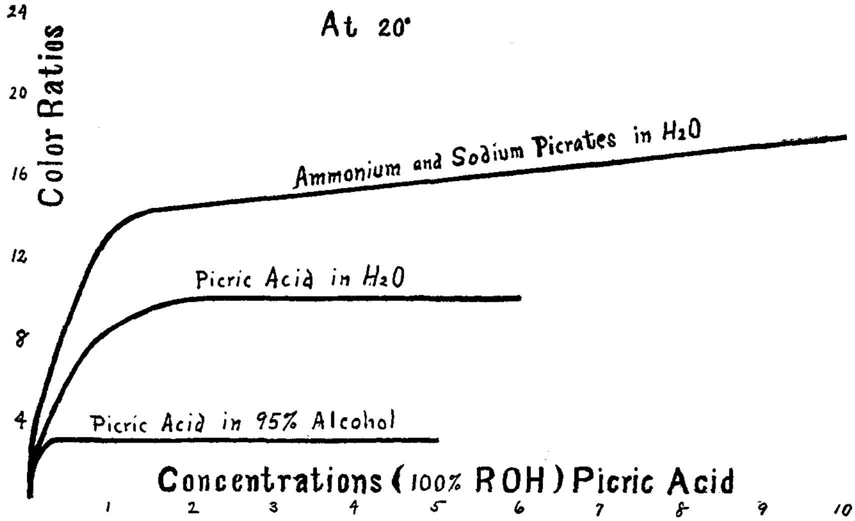

Fig. 1.

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[1] Bredig and Fraenkel, *Ber.*, 39, 1756 (1906); Fraenkel, *Z. physik. Chem.*, 60, 202 (1907); Bredig, *Z. electrochem.*, 18, 535 (1912); Snethlage, *Ibid.*, 18, 539 (1912); Millar, *Z. physik. Chem.*, 85, 129 (1914); Braune, *Ibid.*, 85, 170 (1914); Snethlage, *Ibid.*, 85, 211 (1914).

[2] Bruni and Berti, *Atti accad. Lincei*, [5] 9, 273, 321 (1900).

[3] THIS JOURNAL, 36, 407, 837 (1914). See preceding paper.

[4] The solubility of picric acid in water is given by Dolinski, *Ber.*, 38, 1836 (1905); in ether and benzene by Findlay, *J. Chem. Soc.*, 81, 1219 (1902); in moist ether by Bougault, *J. Pharm. Chem.*, [6] 18, 116 (1903).

The solutions used were picric acid in (1) absolute ethyl alcohol, (2) 95% ethyl alcohol, (3) water, (4) sodium hydroxide, and (5) ammonium hydroxide.

Though picric acid is more nearly colorless in ether, benzene, etc., than in absolute alcohol, solutions of the latter were taken as the basis of comparison of color, for the reasons not only that alcohol is inexpensive and convenient but it has about fifty times as great solvent power as the other solvents.

The anhydrous alcohol used was prepared by the calcium carbide method

TABLE I.

| Absolute alcohol picric acid. | 95% al. picric acid. | Water solution picric acid. | Water sodium picrate. | Water ammonium picrate. | Color ratios. | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | 95% alcohol. | Water picric acid. | Sodium picrate. | Ammonium picrate. |
| 0.001 | 0.0010 | 0.0010 | 0.001 | 0.0010 | 1.0 | 1.0 | 1.0 | 1.0 |
| 0.002 | 0.0020 | 0.0020 | 0.002 | 0.0020 | 1.0 | 1.0 | 1.0 | 1.0 |
| 0.004 | 0.0030 | 0.0030 | 0.003 | 0.0030 | 1.3 | 1.3 | 1.3 | 1.3 |
| 0.006 | 0.0046 | 0.0033 | 0.004 | 0.0040 | 1.3 | 1.8 | 1.5 | 1.5 |
| 0.007 | 0.0050 | 0.0035 | 0.004 | 0.0043 | 1.4 | 2.0 | 1.7 | 1.6 |
| 0.008 | 0.0055 | 0.0040 | 0.005 | 0.0047 | 1.4 | 2.0 | 1.6 | 1.7 |
| 0.009 | 0.0060 | 0.0045 | 0.006 | 0.0050 | 1.5 | 2.0 | 1.5 | 1.8 |
| 0.01 | 0.007 | 0.0050 | ... | 0.0050 | 1.4 | 2.0 | .... | 2.0 |
| 0.02 | 0.010 | 0.0070 | ... | .... | 2.0 | 3.0 | .... | .... |
| 0.04 | 0.020 | .... | 0.010 | .... | 2.0 | .... | 4.0 | .... |
| 0.05 | 0.025 | .... | ... | .... | 2.0 | .... | .... | .... |
| 0.06 | 0.03 | 0.02 | 0.013 | 0.02 | 2.0 | 3.0 | 4.6 | 3.0 |
| 0.08 | 0.04 | .... | ... | .... | 2.0 | .... | .... | .... |
| 0.1 | 0.04 | 0.03 | 0.020 | .... | 2.5 | 3.3 | 5.0 | .... |
| 0.2 | 0.07 | 0.04 | ... | 0.04 | 3.1 | 5.0 | .... | 5.0 |
| 0.3 | 0.1 | 0.05 | ... | 0.05 | 3.0 | 6.0 | .... | 6.0 |
| 0.4 | .... | 0.06 | 0.044 | .... | ... | 6.6 | 9.1 | .... |
| 0.5 | .... | 0.08 | 0.052 | .... | ... | 6.3 | 9.6 | .... |
| 0.6 | 0.2 | 0.09 | 0.060 | 0.06 | 3.0 | 6.6 | 10.0 | 10.0 |
| 0.8 | .... | 0.10 | ... | .... | ... | 8.0 | .... | .... |
| 0.9 | 0.3 | .... | 0.070 | 0.07 | 3.0 | .... | 12.8 | 12.8 |
| 1 | 0.35 | .... | 0.077 | .... | 3.0 | .... | 13.9 | .... |
| 2 | 0.7 | 0.2 | ... | .... | 3.0 | 10.0 | .... | .... |
| 3 | 1.0 | 0.3 | ... | 0.2 | 3.0 | 10.0 | .... | 15.0 |
| 4 | 1.3 | 0.4 | ... | .... | 3.1 | 10.0 | .... | .... |
| 5 | 1.6 | .... | 0.30 | .... | 3.1 | .... | .... | .... |
| 6 | .... | 0.6 | ... | 0.33 | ... | 10.0 | .... | 18.2 |
| 8 | .... | .... | 0.43 | .... | ... | .... | 18.6 | .... |
| 9 | .... | .... | 0.50 | 0.5 | ... | .... | 18.0 | 18.0 |
| 12 | .... | .... | 0.60 | 0.6 | ... | .... | 20.0 | 20.0 |
| 15 | .... | .... | 0.70 | 0.7 | ... | .... | 21.4 | 21.4 |
| 16 | .... | .... | ... | .... | ... | .... | .... | .... |
| 17 | .... | .... | 0.77 | .... | ... | .... | 22.1 | .... |
| 18 | .... | .... | 0.80 | 0.9 | ... | .... | 22.5 | .... |
| 21 | .... | .... | ... | 1.0 | ... | .... | .... | 23.3 |
| 24 | .... | .... | ... | .... | ... | .... | .... | 24.0 |

and consequently contained traces of acetylene. The water used was ammonia free.[1]

By comparing the colors of the different solutions with the absolute alcohol series the following data were obtained. It must be remembered that the horizontal distribution of data signify identity of color; the numbers are the respective concentrations giving equal colors.

## General Observations.

1. At 0.001% concentration, all the differently prepared solutions have the same color.

2. In concentrated solutions, the absolute alcohol has the least color. The others have greater color in the order of 95% alcohol, water, sodium hydroxide, and ammonium hydroxide—the respective color ratios being 3.1, 10, 22.5 and 24.

3. Alcohol molecules have little effect on the picrate color and the alkali molecules have the greatest effect.

4. The transition-concentrations are at about 0.007% concentration as seen in the curves of Figs. 1 and 2.

## Discussion.

Since the quinoid structure of picric acid represents a more highly colored substance than its benzoid structure, a given concentration of quinoid molecules will manifest itself by more highly-colored solutions, and since at low concentrations (0.001%) all the different solutions have the same color, it may be assumed that, at these concentrations, the picric acid molecules exist in identical equilibria of the two isomers, or that all of the acid is in the quinoid form. That only the quinoid isomer exists at these low concentrations, or at least that it predominates, is evidenced[2] by the progressive divergence of color in higher concentrations of the aqueous and alcoholic solutions. Or conversely considered, while the different series of concentrated solutions have different color ratios, they become identical in color and yield a preponderance of quinoid molecules, when the limit of 0.001% concentration is reached. Therefore, if we assume that most of the picrate molecules in the different 0.001% concentrations are in the quinoid form,[3] it is easy to study at higher concentrations the progressive transformations to the benzoid form. Such studies were made and demonstrate that this transformation is influenced by water, by alkalies and by heat.

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[1] If anhydrous solutions of picric acid were strictly colorless, they could not, of course, be used as a basis of comparison for colored solutions.

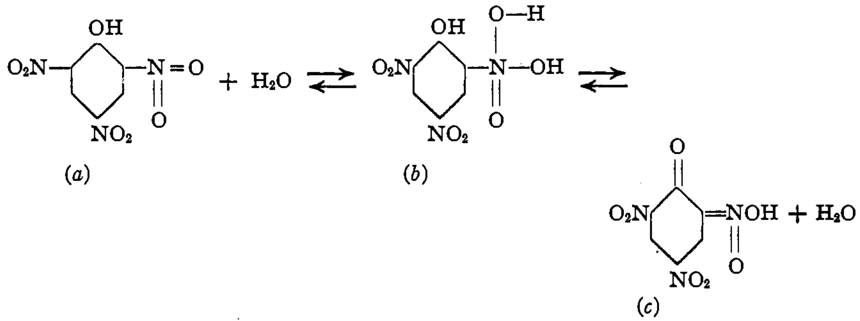
[2] That all of the picrate molecules in the 0.001% concentrations are in the quinoid form seems probable also from the fact that no changes of color are produced by heating such solutions.

[3] Strictly speaking it cannot be maintained that the higher absolute alcohol concentrations hold all of the picric acid molecules in the benzoid form, for colorless picric acid can be prepared. However, for the purposes of this paper they are so assumed.

**The Influence of Water.**—The influence of water on alcohol solutions of picric acid has been recognized and measured by various investigators.[1] Our experiments show that three times as many quinoid molecules exist in the higher concentrations of the 95% alcohol, and ten times as many in the higher concentrations of water, as in the absolute alcohol.

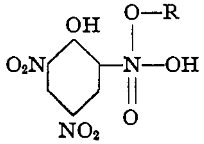
That all picric acid molecules in concentrated aqueous solutions are not in the quinoid form is evidenced by the further deepening of color of such solutions when treated with alkalies or when heated.

Since the quinoid form is favored by aqueous dilution and the benzoid form by aqueous concentrations, it is evident[2] that hydration and dehydration[3] are the processes involved in such transformations. Starting, therefore, with white anhydrous picric acid or with concentrated solutions of the colorless form, we can assume that the following changes[4] result when such are diluted:

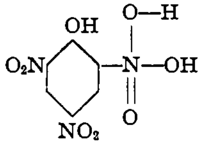


(a) (b) (c)

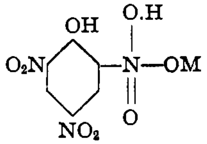
and the reverse, when concentrated or dehydrated. That is, while both isomeric forms are present in the various aqueous solutions, the equilibrium is driven toward the quinoid form, either by alkalies, heat, or by the mass influence of water. It is possible that solutions contain variations of form (b), that is, with alcohol, water, and the alkalies, the following structures may first exist:



(d)



(b)



(e)

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[1] See Bortini, *Z. physik. Chem.*, 87, 104 (1914), for bibliography, experiments and discussion.

[2] When white crystals of picric acid, either alone or in contact with oily pyrophosphoric acid, are treated with absolute alcohol or with water, yellow solutions are produced, thus *showing isomerization toward the yellow quinoid form, even in the presence of hydrogen ions.*

[3] See paper on the mass influence of water on dyes.

[4] Of course, the para nitro group may react in a similar manner, and indeed it may be the only nitro group that does react.

and such conditions as tend to remove alcohol or water, namely heat will increase the yield of the quinoid form.

**The Influence of Alcohol** on the benzoid-quinoid equilibrium is similar to that of water, but is less intense. Since heat increases the color of all the alcoholic solutions, a change of (*d*) to (*c*) is evident; that this is less than that of the change of (*b*) to (*c*), is proven by the fact that the colors of all aqueous solutions are deeper than that of equivalent alcohol solutions.

**The Influence of Alkalies** is greater than that of water, the limit of their color ratio being 24:10. In other words, it may be stated that (*e*) loses water 2.4 times as readily as (*b*).

Since the color ratios of sodium hydroxide and ammonium hydroxide run strictly parallel, it may be stated that the loss of water from (*e*) is independent of the metallic content of the —NOM group.[1]

Furthermore, since alcohol, water, ammonium hydroxide and sodium hydroxide differ widely in degrees of ionization, while their color ratios differ within the narrow limits of 1–24, and since the same solute is involved, it may be concluded that *the picrate color changes are not primarily influenced by the concentration of ions.*

**The Influence of Dilution,** in all cases, is to give the same equilibrium (in 0.001% concentration). This may be interpreted as the *final mass influence of the solvent,* converting (*a*), (*b*), (*d*) and (*e*) into (*c*). Since at 0.001% concentration, 100 g. of water would be present with 0.001 g. of picric acid, 7860 mols. $H_2O$ would be present for each mol. of the picric

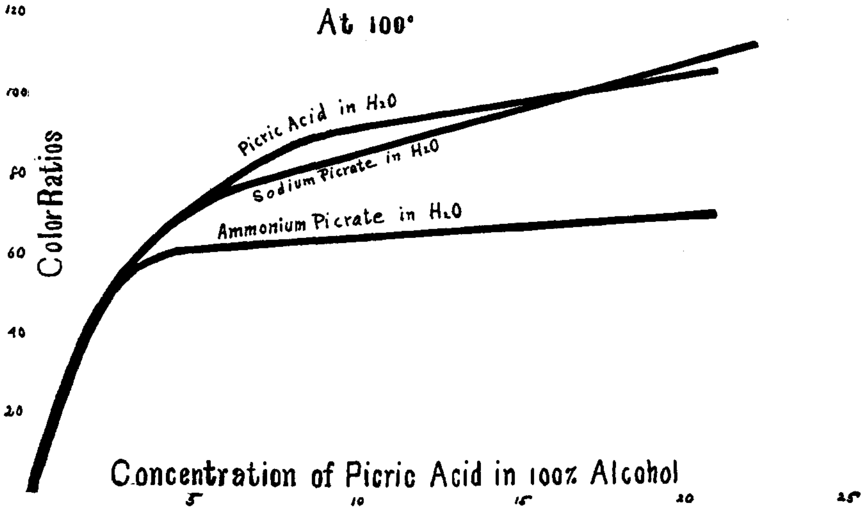

Fig. 2.

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[1] See, however, the effect of heat on these solutions.

acid. This, then, is approximately the mass of water[1] necessary to transform (*a*) into (*c*). The mass of alcohol, calculated in the same manner, is found to be approximately 20000 molecules.

## The Influence of Heat.

Bottles tightly stoppered and containing the various solutions were heated in actively boiling water baths. The resulting increased colors were measured at once by comparing with members of the cold alcohol series. Since the absolute alcohol series did not always furnish sufficient depth of color, comparisons were made against one or more 95% alcohol solutions and the readings thus obtained were interpolated to readings of the absolute alcohol series. In this manner the following data were obtained:

SOLUTIONS HEATED TO 100°.

| Concentrations of heated | | | Matched with cold | | Color ratios of | | |
|---|---|---|---|---|---|---|---|
| Aq. pic. | Aq. Na-pic. | Aq. $NH_4$-pic. | 100% ROH. | 95% ROH. | Aq. pic. | Aq. Na-pic. | Aq. $NH_4$-pic. |
| 0.001 | 0.001 | 0.001 | 0.002 | 0.002 | 2.0 | 2.0 | 2.0 |
| ... | ... | 0.002 | 0.008 | 0.005+ | ... | ... | 4.0 |
| ... | 0.003 | ... | 0.120 | 0.008 | ... | 4.0 | .... |
| ... | ... | 0.003 | 0.180 | 0.009 | ... | ... | 5.2 |
| ... | ... | 0.004 | 0.032 | 0.01+ | ... | ... | 8.0 |
| ... | 0.005 | ... | 0.033 | 0.01+ | ... | 6.6 | .... |
| 0.003 | ... | ... | 0.040 | 0.020 | 1.3 | ... | .... |
| 0.005 | ... | ... | 0.047 | 0.02+ | 9.0 | ... | .... |
| ... | 0.007 | ... | 0.058 | 0.030 | ... | 8.3 | .... |
| ... | ... | 0.006 | 0.075 | 0.03+ | ... | ... | 12.5 |
| 0.007 | ... | ... | 0.080 | 0.040 | 11.4 | ... | .... |
| ... | ... | 0.008 | 0.135 | 0.04+ | ... | ... | 16.5 |
| ... | ... | 0.010 | 0.180 | 0.060 | ... | ... | 18.0 |
| 0.010 | ... | ... | 0.200 | 0.06+ | 34.0 | ... | .... |
| ... | 0.020 | ... | 0.600 | 0.200 | ... | 30.0 | .... |
| ... | ... | 0.030 | 0.900 | 0.300 | ... | ... | 30.0 |
| 0.030 | ... | ... | 1.200 | 0.400 | 39.0 | ... | .... |
| ... | ... | 0.040 | 1.440 | 0.500 | ... | 36.0 | .... |
| 0.050 | ... | ... | 2.250 | 0.7+ | 45.0 | ... | .... |
| ... | ... | 0.050 | 2.400 | 0.800 | ... | ... | 48.0 |
| ... | 0.060 | ... | 2.850 | 0.9+ | ... | 50.0 | .... |
| ... | ... | 0.070 | 4.200 | 1.000 | ... | ... | 60.0 |
| 0.070 | 0.080 | 0.090 | 6.000 | 2.000 | 74.0 | 75.0 | 60.0 |
| 0.090 | ... | ... | 7.500 | 2.500 | 87.0 | ... | .... |
| 0.100 | ... | ... | 9.000 | 3.000 | 90.0 | ... | .... |
| 0.200 | ... | 0.300 | 21.000 | 7.000 | 105.0 | ... | 69.0 |
| ... | 0.200 | ... | 22.000 | 7.500 | ... | 111.0 | .... |

That the color of all picrate solutions is increased by heat may be accounted for by the kinetic decomposition of forms (*b*), (*d*) and (*e*) to yield greater concentrations of the quinoid form (*c*). Whereas cold

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[1] THIS JOURNAL, 36, 841 (1914). Note that one molecule of $K_2Cr_2O_7$ is changed to chromate by 131000 mols. $H_2O$.

solutions of the sodium and ammonium picrates show parallel intensities of color, they diverge rapidly at 100°. This may be accounted for either on the basis of a decomposition of the ammonium salt by heat or on the basis that the sodium and ammonium salts may possess different transition-concentrations at the higher temperatures. Furthermore, it is not clear why the heated ammonium picrate series should show less intense colors at 100° than the aqueous solutions. This phenomena, the progressive influence of heat on picrates and *o*-nitro phenolates, and other studies of the latter will be made.

## Summary.

1. Color changes of picrate solutions are produced by changes of concentration, temperature and alkalinity.

2. Color ratios were measured and correlated in curves.

3. The order of reagents and conditions increasing the color are: HCl, 100% alcohol, 95% alcohol, alkalies and heat.

4. Picric acid probably exists in two isomeric forms; changes of color are explained on the basis of disturbance of its benzoid-quinoid equilibrium.

5. Deviations from Beers' law are also quite satisfactorily accounted for.

SEATTLE, WASH.

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CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WASHINGTON.]

# FALLACIES IN COLORIMETRY.

BY WILLIAM M. DEHN.

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In colorimetric experiments certain factors introducing variations and errors[1] are frequently overlooked—chief among these are variable sensitiveness[2] of vision to different concentrations and the bicolored nature of the solution.

In most colorimetric determinations,[3] the depths of solutions of the color standards are matched by various depths and concentrations of the solutions to be estimated; usually we have two columns of solutions of unequal length whose tints are matched to the limit of sensitiveness of the eye and whose solute molecules are assumed to be the same in number. That the solute-molecules are not necessarily the same, not only in number but in composition, may be concluded from studies of (1) their different

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[1] For a discussion of colorimetric methods, see THIS JOURNAL, 27, 1192.

[2] Horn, *Am. Chem. J.*, 35, 253; Horn and Blake, *Ibid.*, 36, 195, 516. These authors discuss variable sensitiveness in colorimetry. They show that, with equal depths "at certain definite concentrations, the comparisons in colorimetric determination of chromium can be made with greater ease and accuracy than at other concentrations," and it is held by them that this relation is "perfectly general throughout colorimetry."

[3] Scores of colorimeters varying from simple vials and test tubes to complicated