Wagner-Jauregg reported that they could not detect any trace of a fluorescence spectrum of phosgene exciting with mercury lines in the region of the sharp bands. Now Herzberg[11] and others have shown that the absence of fluoresence is probably the best criterion of predissociation. Therefore it is very probable that predissociation is occurring at longer wave lengths than the limit of 2700 Å. given by Henri. The second fact that points to this same conclusion is that the sharp bands are superimposed on a continuous absorption and some measurements by Kuhn and Martin[12] at $\lambda = 2816$ Å. attribute 76% of the absorption at that wave length to the continuum which undoubtedly results in dissociation. On the basis of these observations we feel justified in saying that our mechanism applies to the decomposition at all wave lengths absorbed by phosgene.

Summary

The photochemical decomposition of phosgene has been studied kinetically and a reaction mechanism has been proposed from which the rate law

$$-\mathrm{d}(\mathrm{COCl_2})/\mathrm{d}t = kI_{\mathrm{abs.}} - k'I_{\mathrm{abs.}}^{1/2}(\mathrm{CO})^{1/2}(\mathrm{Cl_2})$$

may be derived. It has been shown that this rate law represents the experimental facts and that the mechanism is in accord with the previous work on phosgene photochemical reactions. The work of Almasy and Wagner-Jauregg has been discussed and a possible explanation presented.

BERKELEY, CALIF. RECEIVED FEBRUARY 10, 1934

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[11] Herzberg, *Ergebnis der exakt. Naturwiss.*, **10**, 207 (1931).

[12] Kuhn and Martin, *Z. physik. Chem.*, **B21**, 93 (1933).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

New Indicators for Oxidimetry: Some Phenanthroline and Diphenylamine Derivatives[1]

BY LOUIS P. HAMMETT, GEORGE H. WALDEN, JR., AND SYLVAN M. EDMONDS

The ability to titrate to or from a visual end-point representing any one of a series of definite oxidation potentials which differ by moderate intervals should be of advantage in the use of oxidimetry in analytical chemistry. Toward the goal of developing the necessary series of mobile, reversible oxidation indicators the present article offers some progress. The starting points were the already known phenanthroline ferrous[2] and diphenylamine[3] indicators.

Phenanthroline Derivatives

The intense color of the phenanthroline ferrous complex is entirely lacking in the known complexes of phenanthroline with nickel, cobaltous, cupric, zinc and cadmium ions.[4] Nor have we found it possible to oxidize or to reduce these complexes to intensely colored products. The addition of phenanthroline to a solution of chromous acetate produces a red solution which undergoes a sharp and reversible change to reddish-violet with oxidants in acid solution, presumably because of oxidation to a chromic compound. From the behavior of the oxidized compound with ferrous ion it appears that the potential of this system is not very different from the ferric–ferrous potential. The shift of some three-quarters of a volt upward which the chromic–chromous system undergoes when complex formation with phenanthroline takes place is of theoretical interest, but the compounds have no value as indicators, because the color intensity is not high and color contrast at the end-point is not great.[5]

Nitrophenanthroline Ferrous Ion.—We have obtained a hitherto unknown nitrophenanthroline by the following procedure. One gram of *o*-phenanthroline was dissolved in 10 cc. of concentrated nitric acid, and the solution was added to 20 cc. of 95% sulfuric acid. After one hour at 115–120°, the product was precipitated by dilution with water and addition of sodium hydroxide. It was recrystallized from water: melting point

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[1] This article is based mainly upon part of a dissertation submitted by Sylvan M. Edmonds to the Faculty of Pure Science of Columbia University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, May, 1933.

[2] (a) Walden, Hammett and Chapman, THIS JOURNAL, **53**, 3908 (1931); **55**, 2649 (1933); (b) Walden, Hammett and Edmonds, *ibid.*, **56**, 57 (1934); (c) Walden, Hammett and Edmonds, *ibid.*, **56**, 350 (1934).

[3] (a) Knop, *ibid.*, **46**, 263 (1924); (b) Willard and Young, *Ind. Eng. Chem.*, **20**, 764 (1928); (c) Willard and Young, THIS JOURNAL, **50**, 1334 (1928); (d) Sarver and Kolthoff, *ibid.*, **53**, 2902 (1931).

[4] Blau, *Monatsh.*, **10**, 372 (1889); **19**, 647 (1898).

[5] Barbieri and Tettamanzi, *Atti Accad. Lincei*, **15**, 877 (1932), have reported recently on the chromous dipyridyl complex, but the phenanthroline complex seems not to have been observed previously.

202°, yield 0.33 g. *Anal.* Calculated for $C_{12}H_7N_3O_2$: C, 63.97; H, 3.14; N, 18.67. Found: C, 64.29; H, 2.72; N, 19.23.

The intensely red nitrophenanthroline ferrous ion is formed by direct reaction of ferrous salt and the base, even in the presence of appreciable concentrations of strong acids. It is therefore decidedly more stable toward acids than the corresponding phenanthroline complex, which is quite completely though only slowly decomposed by strong acids. The two complexes also differ in color, the nitro compound being of a somewhat bluer shade. The equilibrium between the new complex and hydrogen ion is largely affected by temperature, and a dilute acid solution loses its color when heated to boiling but recovers it on cooling.

Ceric sulfate in acid solution converts the red color to a greenish-blue of relatively low intensity, presumably by oxidation to the ferric complex. A direct determination of the oxidation potential by potentiometric titration failed because the potential rose after each increment of oxidant only to fall rapidly to nearly the original value. We have also noted that immediate addition of ferrous sulfate to a freshly oxidized solution regenerates the red color instantaneously, while the color appears only slowly if a few minutes are allowed to elapse between the oxidation and the addition of ferrous ion. These phenomena are in agreement with the hypothesis that the ferric complex is rapidly decomposed by acids into ferric ion and nitrophenanthrolinium ion with resultant decrease in potential. Addition of ferrous ion before this reaction is complete reduces the ferric complex instantaneously to the ferrous, later addition of ferrous ion forms the ferrous complex by slow reaction of ferrous ion with nitrophenanthrolinium ion.

The following facts show, however, that the nitrophenanthroline ferrous potential is appreciably higher than the phenanthroline ferrous potential. When the nitro complex is used as indicator for the titration of ferrous ion with ceric ion in 1 *m* sulfuric acid, the end-point is not sharp and an excess of 3 parts per thousand of ceric ion is necessary for complete disappearance of the red color. Also the nitro complex is apparently unaffected by vanadic acid in 1 *m* sulfuric acid, while phenanthroline ferrous ion is oxidized. From the excess of ceric ion required for an end-point and some experiments on color intensity it is possible to estimate the molar potential of the new complex in this acid concentration to be 0.19 volt lower than the ceric–cerous potential, hence 0.11 volt above the phenanthroline ferrous potential. This removes any doubts which may have been aroused by the practical identity of the phenanthroline ferrous and the dipyridyl ferrous potentials of the possibility of producing significant changes in the potential of these metal complexes by substitution in the organic part.

Diphenylamine Derivatives

***p*-Nitrodiphenylamine** is oxidized by ceric ion to an intensely reddish-violet compound. As an indicator it shares with diphenylamine and its sulfonic acid[3d] the disadvantages of destruction by excess oxidant and complicated reaction mechanism.[6] It has however a potential so high that it may be used in the oxidimetric titration of ferrous ion, whereas diphenylamine is satisfactory only when the ferrous potential has been lowered by addition of fluoride or other former complex.[7] The color change at the end-point is extremely sharp and vivid. In the titration with ceric sulfate of 25 cc. of approximately 0.1 *m* ferrous sulfate in 200 cc. of 1 *m* sulfuric acid using 2 drops of 0.01 *m* solution of *p*-nitrodiphenylamine in glacial acetic acid as indicator, a ratio of 0.9925 with an average deviation of 0.2 part per thousand was obtained in five titrations. With phenanthroline ferrous indicator a ratio of 0.9921 was obtained. Because of irreversible oxidation of the indicator the reverse titration of ceric ion with ferrous ion is unsatisfactory, and the dichromate–ferrous titration is unsatisfactory because of slow reaction.

The oxidation potential was determined by titrating ferrous sulfate in 1 *m* sulfuric acid containing the indicator with ceric sulfate to a visual end-point, and immediately measuring the potential. In four separate measurements a value of 0.29 ± 0.02 volt against quinhydrone in the same acid was obtained. The substitution of the nitro group has therefore raised the potential of diphenylamine by some 0.3 volt.[6]

Evidently the introduction of a second nitro group raises the potential necessary for oxidation still higher, for the following were found to undergo no visible color change with ceric or permanganate ions or with sodium bismuthate in acid solution: 2,4-dinitrodiphenylamine, 2,4,6-trinitrodiphenylamine, 2,4,6,3′-tetranitrodiphenylamine, 2,4-dinitrophenylbenzidine, 2,4-dinitro-4′-methoxydiphenylamine and 2,4-dinitro-4′-aminodiphenylamine.[8]

***p*-Aminodiphenylamine** can be oxidized to an intensely reddish-violet compound, which is reversibly reduced to a colorless product, but is easily destroyed by excess of oxidant. The potential for the color change in 1 *m* sulfuric acid is apparently somewhat below the ferric–ferrous potential. *p*-Acetylaminodiphenylamine is oxidized by ceric sulfate to a greenish-blue which is more stable toward excess oxidant than is the product from the non-acetylated

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(6) Kolthoff and Sarver, THIS JOURNAL, **52**, 4179 (1930).

(7) Schollenberger, *ibid.*, **53**, 88 (1931).

(8) These substances were prepared by well-known methods from the corresponding aniline and polynitrochlorobenzene derivatives.

base, but is still unsatisfactory for indicator use. From its behavior toward mixtures of varying proportions of ferric and ferrous ions in 1 *m* sulfuric acid, its effective oxidation potential may be estimated at 0.06 below the molar ferric–ferrous potential.

2,4-Diaminodiphenylamine[9] is oxidized by ceric sulfate to a red compound which is only very slowly acted upon by excess of oxidant. An electrometric titration gave a sharp end-point at two equivalents of ceric ion to one of the diaminodiphenylamine. Two equivalents of titanous ion were likewise consumed in an electrometric reduction to a colorless solution. From these titrations (which were repeated with excellent agreement) the molar potential in 1 molar sulfuric acid referred to quinhydrone in the same solution is −0.06. An indicator with a potential in this range, stable toward strong oxidants and acids, seems not previously to have been known.

Reduction with tin and hydrochloric acid of 2,4-dinitro-4′-aminodiphenylamine and of 2,4-dinitro-4′-methoxydiphenylamine yields products with indicator properties practically identical with those of diaminodiphenylamine. The reduction product of 2,4-dinitrophenylbenzidine has indicator properties but is irreversibly oxidized by a small excess of oxidant. The products from 2,4,6-trinitrodiphenylamine and from 2,4,6,3′-tetranitrodiphenylamine show no indicator properties with ceric sulfate.

TABLE I

SUMMARY OF RELATIVE MOLAR OXIDATION POTENTIALS IN 1 *m* SULFURIC ACID AGAINST THE QUINHYDRONE ELECTRODE IN THE SAME ACID

Ceric–cerous[2a]		+0.65
Vanadate–vanadyl[2b]		+ .33
Ferric–ferrous[2a]		− .01
Vanadyl–vanadous[2b]		− .33
Ferrous–phenanthroline[2a]		+ .36
Ferrous–nitrophenanthroline		+ .47
p-Nitrodiphenylamine		+ .29[a]
Diphenylamine sulfonic acid[3d]	*ca.*	+ .1[a]
Diphenylamine[6]	*ca.*	[a]
Diaminodiphenylamine		− .06

[a] These are effective, not molar potentials.

Summary

The relative oxidation potentials and indicator properties of certain derivatives of phenanthroline and diphenylamine have been investigated. Some of these are useful oxidation indicators and cover new potential ranges.

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[9] Prepared by reduction of the dinitro compound with tin and hydrochloric acid. The product agreed in properties with the description of Nietzki and Almenrader, *Ber.*, **28**, 2969 (1895).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, JOHNS HOPKINS UNIVERSITY]

x-Ray Studies of the System Nickel–Oxygen–Water. III. The K-Absorption Limits of Nickel in Various Oxide-Hydrates*

BY R. W. CAIRNS[1] AND EMIL OTT

Introduction

The positions of the principal absorption edges of the elements depend to an appreciable extent on the nature of the chemical bonds by which they are combined with other atoms. In the case of the lighter elements such as phosphorus, sulfur and chlorine, the magnitude of the effects is sufficient to show the influence of factors such as valence, size of surrounding atoms, crystal structure and degree of hydration. Valence changes of the absorbing element produce the largest observed displacements, causing wave length shifts of more than 20 X. U. in the case of chlorine, and a lessening effect as the atomic number of the absorber increases.

Lindsay and Voorhees[2] have measured the Fe K-absorption limits of a number of iron compounds, and have reported wave length shifts $\Delta\lambda$ for di- and trivalent iron as compared to the position of the limit for the pure element as follows

Valence state	Absorber	$\Delta\lambda$ in X. U.
II	$FeCO_3$	1.4
	$FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$	1.9
II and III	Fe_3O_4	1.9
	$FeSO_4(NH_4)_2SO_4 \cdot 6H_2O + FeCl_3 \cdot 6H_2O$	1.8
III	$FeCl_3 \cdot 6H_2O$	2.5
	Fe_2O_3	2.5

These results are quoted here in detail since we may anticipate quite comparable results for our present investigation on nickel, due to the close relationship of the two elements in question.

There has been some doubt in the past as to the valence of nickel in certain so-called oxide-hydrates. An investigation of the properties of several of these compounds was recently reported by the authors.[3] In particular, the existence of a compound having the empirical formula $Ni_2O_3 \cdot$

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* Presented in part at the Washington Meeting of the American Chemical Society, 1933.

[1] Firestone Tire and Rubber Company Fellow, 1929–1933.

[2] Lindsay and Voorhees, *Phil. Mag.*, [7] **6**, 910 (1928).

[3] Cairns and Ott, THIS JOURNAL, **55**, 527, 634 (1933).