[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

OXIDATION OF HYDRAZINE
VIII. MONO-DELECTRONATORS AND DI-DELECTRONATORS[1]

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Among the objectives of the current series of investigations have been (1) an elucidation of the mechanism involved in the oxidation of hydrazine and (2) a general classification of oxidizing agents,[2] possibly valid also in other reactions.

When the attempt is made to group oxidants together on the basis of their behavior toward hydrazine, it is found that substances of widely divergent oxidation potentials fall into the same category. It has been shown by extended experiments that the peroxide, permanganate and manganic ions, all of high potential, give distinctly different results when brought into contact, under similar conditions, with hydrazine ions in the presence of sulfuric acid. Hydrogen peroxide yields large amounts of both hydronitric acid and ammonia;[1a,1d,1f] potassium permanganate, small amounts of hydronitric acid and large amounts of ammonia;[1d] and manganic acetate no hydronitric acid but large amounts of ammonia.[3] On the other hand, the arsenate ion yields hydronitric acid and ammonia,[1e] while the cupric ion, of similar potential, gives ammonia but no hydronitric acid.[1e]

On the basis of these facts, hydrogen peroxide and arsenic acid would be grouped together, despite the marked disparity in their oxidizing power. Similarly, manganic and cupric salts would be placed in the same class. These instances are fairly typical of the large number that might be adduced.[4]

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[1] For the earlier articles of this series see (a) Browne, THIS JOURNAL, **27**, 551 (1905); (b) Browne and Shetterly, *ibid.*, **29**, 1305 (1907); (c) **30**, 53 (1908); (d) **31**, 221 (1909); (e) **31**, 783 (1909); (f) Hale and Redfield, **33**, 1353 (1911); (g) Hale and Nunez, **33**, 1555 (1911); (h) Browne and Overman, **38**, 285 (1916). The present work is based upon a part of the thesis presented to the Faculty of the Graduate School of Cornell University by R. E. Kirk, Grasselli Fellow in Chemistry, 1926–1927, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

This article is respectfully dedicated by the authors to Professor L. M. Dennis, and will be reprinted as Article No. 6 in the Louis Munroe Dennis Quarter Century Volume to be published in 1928 in commemoration of the completion by Professor Dennis of twenty-five years of service as Head of the Department of Chemistry at Cornell University.

[2] Ref. 1 e, p. 797.

[3] Bray and Cuy, THIS JOURNAL, **46**, 1796 (1924).

[4] Against the possible vague contention that this anomalous collocation of dissimilar oxidants might be attributed to specific catalytic effects may be cited the fact that both positive and negative ions are included in each of the groups concerned. It would be difficult to conceive of a catalytic process sufficiently broad in its scope to cover all of the cases under consideration.

Oxidation and Reduction as Delectronation and Electronation

It was stated in 1903 by J. J. Thomson[5] that: "A univalent electro-positive atom is one which under the circumstances prevailing when combination is taking place, has to lose one and only one corpuscle, before stability is attained; a univalent electro-negative atom is one which can receive one, but not more than one, corpuscle without driving off other corpuscles from the atom; a divalent electro-positive atom is one that loses two corpuscles and no more, and so on."

In the same year, Abegg[6] expressed more definitely the ideas first pre-adumbrated by Berzelius,[7] and later outlined by Ostwald,[8] concerning the relationship between chemical action and .electric charges. The close correspondence now recognized between chemical and electrochemical actions is a logical outgrowth also of the epochal discoveries of Faraday.[9] According to Bancroft,[10] "The most striking characteristic of an electrolytic reaction is that it occurs in two places—at the anode and at the cathode. The peculiarity can be made less marked by bringing the electrodes nearer and nearer together. When the distance between them vanishes, we have a chemical reaction in the ordinary sense of the word, and not an electrochemical reaction."

The view that oxidation and reduction involve a transfer of electrons has been widely disseminated by Alexander Smith[11] and by Stieglitz,[12] who also extended the idea to the oxidation of organic substances. Similar concepts have been employed by Falk and Nelson,[13] by Fry,[14] and by L. W. Jones[15] and their associates to explain organic reactions.

The reasons for considering the fundamental mechanism in reactions of oxidation and reduction to involve a transfer of electrons have been carefully reviewed by Cady and Taft,[16] who believe that "in the absence of any proof to the contrary, the most convenient and the most generally

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[5] Thomson, Silliman Lectures at Yale University, published under title "Electricity and Matter," Scribners, New York, **1905**.

[6] Abegg, *Z. physik. Chem.*, **43**, 385 (1903); *Z. anorg. Chem.*, **39**, 330 (1903).

[7] Berzelius, "Lehrbuch der Chemie," Erster Band, Arnold'sche Buchhandlung, Dresden and Leipzig, **1843**, p. 105, 110.

[8] Ostwald, "The Scientific Foundations of Analytical Chemistry," 1st ed., trans. by McGowan, Macmillan Company, New York, **1895**, pp. 90–98.

[9] Faraday, "Experimental Researches," Vol. I, Series III, §8, p. 102; Series VII, §11, p. 1195.

[10] Bancroft, *Trans. Am. Electrochem. Soc.*, **8**, 33 (1905); **9**, 13 (1906).

[11] Smith, "General Chemistry for Colleges," The Century Co., New York, **1916**, p. 322.

[12] Stieglitz, "Qualitative Chemical Analysis," The Century Co., New York, **1911**.

[13] Falk and Nelson, This Journal, **37**, 1732 (1915).

[14] Fry, *ibid.*, **37**, 2368 (1915).

[15] L. W. Jones, *ibid.*, **39**, 674 (1917).

[16] Cady and Taft, *J. Phys. Chem.*, **29**, 1057, 1075 (1925).

correct view is to regard the process as a direct transfer of charges..., a conception which is also in accord with the present electronic theory of valence. It must be understood that we are advancing no arguments against the formation of intermediate *compounds* in oxidation and reduction reactions, as there is experimental evidence on record in so large a number of cases that this is not a question for argument."

Direct evidence of reduction effected by electrons supplied either from a spark cathode or by the β-radiation from radium, and of oxidation effected by α-particles from radium has been presented by Pisarzhevskii and Rosenberg.[17] The restoration of electrostatic equilibrium through certain membranes that show ionic selectivity has been demonstrated by Girard and Platard[18] to occur as the result of a transfer of electrons rather than of ions.

On the basis of such experimental evidence as the foregoing, it seems reasonable to conclude that oxidation is to be regarded as essentially a process of *delectronation*,[19] and reduction as *electronation*.

Mono-Delectronators and Di-Delectronators

Oxidizing agents may be grouped in two classes: (1) those that accept one electron only per active unit (atom, ion or molecule) and (2) those able to accept more than one electron per active unit. Members of the first class, including such oxidants as ferric, manganic, ceric and cupric ions, may be termed *mono-delectronators*. The second class comprises *di-delectronators*[20] such as peroxide, chlorate and persulfate ions, as well as possible *tri-delectronators* and other *poly-delectronators*.[21]

Oxidation of Hydrazine by Mono-delectronators.—Hydrazine may be completely oxidized, under appropriate conditions, to nitrogen and water. Whenever its oxidation by mono-delectronators is incomplete, the sole by-product formed is ammonia. This may be most readily explained by assuming initial liberation of univalent N_2H_3 residues, or free radicals, each of which contains an atom of bivalent nitrogen, in accordance with the equation

$$N_2H_5^+ - \ominus = N_2H_3 + 2H^+ \qquad (1)$$

Subsequent condensation of two such residues would yield tetrazane, $NH_2.NH.NH.NH_2$, a compound of which organic derivatives have long

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[17] Pisarzhevskii and Rosenberg, *J. Russ. Phys.-Chem. Soc.*, **54**, 533, 548, 570 (1923); *C. A.*, **18**, 1424, 2835 (1924).

[18] Girard and Platard, *Compt. rend. soc. biol.*, **90**, 932, 933, 1020 (1924).

[19] "Delectronation" seems to the authors more euphonious than "de-electronation," which has been proposed by Cady and Taft [*Science*, **62**, 403 (1925)].

[20] "Mono-delectronator" and "di-delectronator" were first suggested in this Laboratory by E. W. Phelan in place of the rather cumbersome terms one-equivalent oxidizing agent and two-equivalent oxidizing agent.

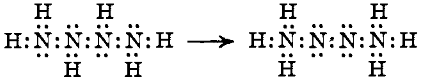
[21] A similar classification of reducing agents as *mon-electronators*, *di-electronators*, and *poly-electronators* is also possible.

been known.[22] Decomposition of this intermediate product would undoubtedly take place with formation of ammonia and nitrogen:

$$N_4H_6 = N_2 + 2NH_3 \qquad (2).$$

The first of these stages, that of delectronation, must be a reaction of the second order, as demonstrated by Bray and Cuy,[3,23] for the oxidation of hydrazine by the typical mono-delectronators, manganic ion and ferric ion. The second and third stages must proceed with greater velocity than the first, as otherwise further delectronation of the residues, either before or after condensation, would be evidenced.

Decomposition of the tetrazane may be conceived to involve a simple migration of two hydrogen nuclei, presumably very mobile, from the central to the external nitrogen atoms of the chain, in accordance with the conventional electronic diagram



$$\mathrm{H{:}\overset{H}{\underset{\cdot\cdot}{\ddot{N}}}{:}\underset{H}{\ddot{N}}{:}\overset{H}{\underset{\cdot\cdot}{\ddot{N}}}{:}\underset{H}{\ddot{N}}{:}H \longrightarrow H{:}\overset{H}{\underset{H}{\ddot{N}}}{:}\underset{\cdot\cdot}{\ddot{N}}{:}\underset{\cdot\cdot}{\ddot{N}}{:}\overset{H}{\underset{H}{\ddot{N}}}{:}H}$$

with ultimate formation of a labile compound of molecular nitrogen and ammonia, $N_2.2NH_3$.

Among the mono-delectronators previously studied in this Laboratory[1e] are ferric, cupric, nickelic and cobaltic ions. Each of these oxidizes hydrazine under the specified conditions with formation of water, nitrogen and ammonia, but no hydronitric acid. The work of Benrath and Ruland[24] upon ceric ion, and that of Bray and Cuy[23] upon manganic and ferric ions show that these oxidants behave in an entirely similar fashion. Manganic ion was found under certain conditions to oxidize hydrazine quantitatively to water, nitrogen and ammonia in conformity with the typical reaction of mono-delectronation.

From the theory just outlined it is predictable that ceric ion, in common with all other mono-delectronators studied, would yield no hydronitric acid as a product of the oxidation of hydrazine. Repeated experiments conducted in this Laboratory, under conditions most favorable for the formation and isolation of the acid, yielded no trace of hydronitric acid, thus confirming the work of Benrath and Ruland. Since Sommer and Pincas[25] and Martin[26] have employed ceric ion for the quantitative oxidation of hydronitric acid, however, it might be urged that this action would account for the non-appearance of the acid as a product of the oxidation of hydrazine. Thiele[27] ascribed the relatively low yields of hydronitric

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[22] Minunni, *Gazz. chim. ital.*, [2] **22**, 217 (1892); [1] **26**, 441 (1896); v. Pechmann, *Ber.*, **26**, 1045 (1893); **27**, 2920 (1894).

[23] Bray and Cuy, This Journal, **46**, 1810 (1924).

[24] Benrath and Ruland, *Z. anorg. Chem.*, **114**, 267 (1920).

[25] Sommer and Pincas, *Ber.*, **48**, 1963 (1915).

[26] Martin, This Journal, **49**, 2133 (1927).

[27] Thiele, *Ber.*, **41**, 2681, 2806 (1908).

acid obtained in various reactions to the "easy oxidizability (leichten Oxydierbarkeit)" of the acid. This suggestion was effectually nullified by the work of Riegger.[28] Nevertheless, it has seemed desirable to obtain direct evidence for the case of the interaction of ceric and hydrazine ions, as to whether putative traces of hydronitric acid would escape oxidation by the ceric ion under the prevailing conditions.

Known amounts of hydronitric acid were introduced beneath the surface of a boiling mixture of ceric sulfate and sulfuric acid in various concentrations. Amounts as small as 0.0001 g. were found to pass through the solution without appreciable loss. This justifies the conclusion that the non-appearance of the acid must be attributed to the inherent character of the reaction, which is clearly one of mono-delectronation.

Oxidation of Hydrazine by Di-delectronators.—Hydrazine may be completely oxidized, under suitable conditions, by certain di-delectronators, at least, to nitrogen and water. In case the oxidation by di-delectronators is incomplete, hydronitric acid is also formed, under favorable conditions, and is invariably accompanied by ammonia. It is probable that bivalent N_2H_2 residues, which may be regarded as free radicals containing either two atoms of bivalent nitrogen or one atom of univalent nitrogen, are first formed in accordance with the equation

$$N_2H_5^+ - 2\ominus = N_2H_2 + 3H^+ \qquad (3)$$

If this process involves the removal of one electron from each of the nitrogen atoms, the $NH.NH$ radical would be formed; the removal of two electrons from one nitrogen, on the other hand, would yield the $N.NH_2$ radical.[29]

Various types of condensation, involving (a) two of these radicals of the same kind, (b) two of different kinds or (c) one of either kind with a molecule of hydrazine, may be considered to occur. Of the five possible bimolecular types only those will be discussed, however, that would yield compounds of which organic derivatives have been prepared.

Condensation of two $N.NH_2$ radicals would yield symmetrical tetrazene, $NH_2.N{:}N.NH_2$, of which numerous organic derivatives, formerly termed tetrazones, have been described.[30] This intermediate product would readily decompose, yielding molecular nitrogen and hydrazine, as follows

$$N_4H_4 = N_2 + N_2H_4 \qquad (4)$$

The formation of nitrogen, primary and secondary amines and aldehydes as decomposition products of the tetra-alkyl tetrazenes, noted by Fischer[31]

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[28] Riegger, This Journal, 33, 1569 (1911).

[29] It is possible that these initial products, instead of being free radicals, as here suggested, may be the much-sought di-imide, $NH{:}NH$, and its unsymmetrical isomer, $N{:}NH_2$, of which the azo compounds and the diazonium compounds are derivatives.

[30] For a comprehensive summary of these compounds see Wieland, "Die Hydrazine," Ferd. Enke, Stuttgart, 1913, p. 38.

[31] Fischer, *Ann.*, 199, 324 (1879).

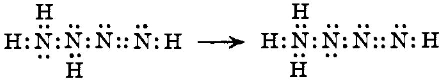
and by Renouf,[32] is explained by Wieland[33] as a result of the formation and subsequent decomposition of the tetra-alkyl hydrazines.

It is probable that all hydrazine molecules that undergo complete oxidation in acid solution to nitrogen and water pass through the stage represented by Equation 4. The relatively large amounts of nitrogen formed in many of the oxidation reactions studied indicate a preferential oxidation of the $N_2H_5^+$ ion to the unsymmetrical residue, $N.NH_2$, rather than to the symmetrical residue, NH.NH. In the case of mono-delectronators, the tetrazane first formed might yield symmetrical tetrazene on further oxidation.[34]

Condensation of two HN.NH radicals might conceivably yield tetrimide, $(NH)_4$, as an intermediate product. This seems unlikely, however, in view of the circumstance that no derivatives of this possible compound have yet been described. Condensation with subsequent rearrangement, possibly by way of aminotri-imide, as suggested by the work of Wohl and Schiff,[35] would result in the formation of unsymmetrical tetrazene, $HN{:}N.NH.NH_2$, of which numerous derivatives, formerly termed buzylenes[36] or diazohydrazines[35] have been prepared. These substances have long been known to yield derivatives of hydronitric acid and ammonia, and it seems inevitable that unsymmetrical tetrazene itself should decompose in corresponding fashion, in the sense of the equation

$$N_4H_4 = HN_3 + NH_3 \tag{5}$$

This decomposition may result from the migration of one hydrogen nucleus from a central to an external nitrogen atom, as indicated in the diagram[37]



$$\mathrm{H:\overset{\displaystyle H}{\overset{..}{\underset{..}{N}}}:\overset{..}{\underset{\underset{\displaystyle H}{..}}{N}}:\overset{..}{N}::\overset{..}{N}:H \longrightarrow H:\overset{\displaystyle H}{\overset{..}{\underset{\underset{\displaystyle H}{..}}{N}}}:\overset{..}{\underset{..}{N}}:\overset{..}{N}::\overset{..}{N}:H}$$

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[32] Renouf, *Ber.*, **13**, 2169 (1880).

[33] Wieland, *Ann.*, **392**, 127 (1912).

[34] Minunni (ref. 22) obtained evidence of the existence of a tetrazane of the type RR'N.NH.NH.NRR', which on oxidation yielded the symmetrical tetrazene, RR'N.N:N.NRR'.

[35] Wohl and Schiff, *Ber.*, **33**, 2741 (1900).

[36] Curtius, *Ber.*, **29**, 759 (1896).

[37] The use of the conventional electronic diagrams as a convenient device for picturing such molecular rearrangements is not to be construed as an acceptance by the authors of the possible implication that hydronitric acid is a non-polar compound, or that the valence of nitrogen, in any ordinary sense of the term, may be two and four in this compound [Langmuir, THIS JOURNAL, **41**, 1543 (1919)]. On the basis of both experimental and theoretical considerations the acid may better be regarded as a polar compound, in which the central nitrogen atom tends to relinquish its five valence electrons, yielding three to the external nitrogen atom and two to the imino group. This finds expression in the formula $\mathrm{H{\rightarrow}N{\leftleftarrows}N{\substack{\rightarrow\\ \rightarrow\\ \rightarrow}}N}$. The N_3^- ion, either in solution or in the crystal lattice of the metallic trinitrides, should possess a symmetrical structure, and the nucleus of the central atom should be equidistant from the nuclei of the outer atoms, each

This would be tantamount to the formation of a labile molecular compound of ammonia and hydronitric acid, $HN_3.NH_3$, isomeric with ammonium trinitride.[38]

Condensation of one $N.NH_2$ with one HN.NH radical and subsequent rearrangement would again result in the formation of unsymmetrical tetrazene, which decomposes in the manner expressed by Equation 5.

Condensation of one $N.NH_2$ or of one HN.NH radical with a molecule of hydrazine should yield, after simple rearrangement, a molecule of tetrazane, which would decompose with formation of nitrogen and ammonia in accordance with Equation 2. This affords a satisfactory explanation of the fact that larger yields of ammonia than of hydronitric acid have been invariably obtained in the oxidation of hydrazine.

Among the di-delectronators previously studied in this Laboratory[1] are peroxide, persulfate, chlorate, bromate, iodate, arsenate, antimonate, selenate, tellurate and molybdate ions. Each of these has been found to oxidize hydrazine under suitable conditions[39] with formation of water, nitrogen, hydronitric acid and ammonia. The reaction of hydrogen peroxide upon hydrazine sulfate has been employed by Browne and Lundell[40] in this Laboratory, and by Martin[26] in the preparation of very pure hydronitric acid.

These experiments attest the validity of the classification, here proposed, for oxidizing agents that have already been investigated. The question now arises as to whether the theory will be of use as a means of predicting the behavior of hitherto unstudied di-delectronators.

Oxidation of Hydrazine by the Di-delectronator, Chlorauric Acid.— It was shown by Lenher[41] that chlorauric acid is reduced by hydrazine, with formation of metallic gold. Gutbier[42] employed hydrazine, and Gutbier and Resenscheck[43] phenylhydrazine in the preparation of gold hydrosols of different colors. No attempt seems to have been made by these investigators to ascertain whether or not hydronitric acid (or phenyl azide) was formed as a product of the reaction.

A solution of chlorauric acid was prepared by dissolving 0.8 g. of gold in aqua regia. Since the presence of oxides, oxy-acids, or oxychlorides

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of which is furnished with eight electrons. This is in conformity with the recent work of Hendricks and Pauling [THIS JOURNAL, **47**, 2904 (1925)] upon the crystal structure of potassium and sodium trinitrides, but contradicts the statement of Carothers [THIS JOURNAL, **45**, 1734 (1923)] that "the structure $R—N=N\equiv N$ is, of course, impossible from the point of view of the octet theory."

[38] Ref. 1 h, p. 288, footnote 1.

[39] In the case of iodate ion no hydronitric acid is formed unless silver sulfate, which serves to prevent the liberation of iodine, is present.

[40] Browne and Lundell, THIS JOURNAL, **31**, 435 (1909).

[41] Lenher, *ibid.*, **35**, 546 (1913).

[42] Gutbier, *Z. anorg. Chem.*, **31**, 448 (1902).

[43] Gutbier and Resenscheck, *ibid.*, **39**, 112 (1904).

of nitrogen might result in the formation of hydronitric acid from hydrazine, thus masking the possible effect of the reagent, scrupulous care was taken to eliminate the last traces of these substances. The purified solution, diluted to 100 cc.; was slowly introduced beneath the surface of a 200cc. portion of a boiling, 0.5% solution of hydrazine sulfate. In two experiments, in which a considerable excess of unoxidized hydrazine remained in the distilling flask, yields of 0.006 and 0.004 g. of hydronitric acid were obtained. The chlorauric acid was quantitatively reduced to metallic gold. The presence of ammonia in the residual solutions was established by qualitative tests.

The formation of hydronitric acid under the conditions just described, which were by no means the most favorable for its production, unequivocally fulfils the prediction concerning the behavior of chlorauric acid. The smallness of the yields is attributable to various factors, including (1) the relatively low concentration of sulfuric acid, (2) the momentary liberation of chlorine during the reaction and (3) the action of aurous ion as a mono-delectronator.

Complex Delectronators.—Oxidizing agents that undergo reduction in two or more stages may in certain cases manifest the characteristics of a mixture of mono- and di-delectronators. The course of the reduction would then be a resultant of the reactions of both types. In such cases it should theoretically be possible, by the use of suitable addition agents, wholly or in part to eliminate one type of reaction, or the other, thus rectifying the complex delectronator, by virtually converting it into a simple mono- or di-delectronator.

An indubitable instance of such rectification is afforded by the work done in this Laboratory[1c] upon the reaction between iodate ion and hydrazine ion in acid solution. This reaction yields iodide ion, readily oxidizable by iodate with liberation of iodine, which in monatomic form is a mono-delectronator. The reaction between iodine and hydrazine evidently takes precedence over that between iodate and hydrazine, with the result that no hydronitric acid is formed. The addition agent, silver sulfate, however, effects removal of the iodide, leaving the iodate ion free to act upon the hydrazine with formation of both hydronitric acid and ammonia.

In case each of the possible stages of a reaction involves simply an accession to the oxidant of the two electrons, the reaction would clearly be one of simple di-delectronation. If, on the other hand, any one of the stages consists in the transfer of a single electron, the reaction is one of complex delectronation.

Potassium permanganate, in its behavior toward hydrazine, affords another instance of complex delectronation. Browne and Shetterly[1d] found that small amounts of hydronitric acid and large amounts of ammonia were formed by the interaction of permanganate and hydrazine ions in acid solution. Since the yields of ammonia were considerably in excess of the values required by Equation 5, the conclusion may be drawn that the principal reaction, aside from that expressed in Equation 4, is one of mono-delectronation, as represented by Equations 1 and 2. This points toward manganic ion, readily formed by interaction of manganous and permanganate ions, as the principal agent. This conclusion is strongly confirmed by the work of Bray and Cuy.[3,23] Any addition agent that would reduce the concentration of manganic ion should increase the yield of hydronitric acid by rectifying the complex reaction to one of simple di-delectronation.[44]

Oxidation of Hydrazine by the Complex Delectronator, Ammonium Metavanadate.—From the work already done in this Laboratory[1b] upon the action of ammonium metavanadate in acid solution upon hydrazine, it is apparent that this reaction is not one of simple di-delectronation. Indeed, at first glance, it would appear, apart from the evidence of the formation of hydronitric acid, to be one of simple mono-delectronation involving reduction of trivalent vanadyl ion (quinquivalent vanadium) to bivalent vanadyl ion (quadrivalent vanadium), as follows

$$VO^{+++} + \ominus = VO^{++} \tag{6}$$

It is probable, however, as suggested by Ditz and Bardach[45] for the reaction between vanadates and hydriodic acid, that a part of the quinquivalent vanadium is directly reduced to trivalent vanadium (univalent vanadyl ion), as follows

$$VO^{+++} + 2\ominus = VO^{+} \tag{7}$$

In this reaction the trivalent vanadyl ion acts as a di-delectronator and is responsible for the formation of hydronitric acid.

It has been shown by the work of Gooch and Gilbert[46] that silver sulfate is reduced by vanadium with a valence of one, two or three, but is not reduced by vanadium with a valence higher than three. The presence of silver sulfate in a reacting mixture of hydrazine and ammonium metavanadate therefore serves to indicate whether or not the vanadium has been reduced below the quadrivalent stage. Metallic silver appears as a product of the reaction in every case where hydronitric acid is formed, and in no case where the acid is not formed. Unless the reduction proceeds beyond the stage represented by Equation 6, therefore, no hydronitric acid is obtained. In a second series of experiments it was found that diminution in the acidity of the solution favors mono-delectronation (Equation 6) and retards di-delectronation (Equation 7), until in a barely acid solution no hydronitric acid whatever is obtained.

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[44] It is possible that addition of soluble sulfates or fluorides for example would produce this result.

[45] Ditz and Bardach, *Z. anorg. Chem.*, **93**, 97 (1915).

[46] Gooch and Gilbert, *Am. J. Sci.*, [4] **15**, 389 (1903).

Oxidation of Hydrazine by Chlorine, Bromine and Iodine.—In the nascent or monatomic condition the halogens are without doubt to be classified as mono-delectronators. Under such conditions that the diatomic molecules, the positive ions (Cl^+, Br^+, I^+), or the ions of the hypoacids (OCl^-, OBr^-, OI^-) constitute the active units, however, the halogens should be capable of functioning as di-delectronators. Earlier observations[1c] of the formation of small amounts of hydronitric acid from hydrazine by the action of chlorine and bromine confirm this supposition. The issue is complicated, however, by the possibility that halogenation may occur, with formation of halogenated residues as intermediate products, which may behave very differently from the radicals liberated by other oxidizing agents.

Chattaway[47] has investigated the action of chlorine and of bromine upon certain primary aromatic hydrazines, and has obtained various halogen substitution products of these substances. In so far as the decomposition of these compounds has been studied it would appear strictly analogous to the decomposition of the corresponding derivatives of free hydrazine to form nitrogen gas and hydrogen chloride.

Despite the probable predominance of halogenation in the oxidation of hydrazine by the free halogens, small amounts of hydronitric acid and ammonia may nevertheless be obtained under suitable conditions, indicating that di-delectronation must occur to some extent during the process.

Experiments in which freshly prepared chlorine water was introduced beneath the surface of a boiling 1% solution of hydrazine sulfate containing one-half of its volume of concentrated sulfuric acid, yielded appreciable amounts of hydronitric acid and ammonia, both in the absence and in the presence of silver sulfate. With bromine smaller yields, found to vary directly with the concentration of the sulfuric acid and to increase in the presence of silver sulfate, were obtained.

With iodine detectable amounts of hydronitric acid were formed only in the presence of silver sulfate. The probable effect of the addition of silver sulfate is to reduce the concentration of iodide ion and thus to favor the formation of iodous ions (I^+). Increase in the acidity of the solution would undoubtedly produce the same effect. The iodous ion, obviously a di-delectronator, is capable of yielding hydronitric acid under favorable conditions, but the necessarily low concentration of the ion precludes the formation of more than small amounts of this product.

Summary

A classification of oxidizing agents (and reducing agents) has been suggested on the basis of the number of electrons transferred per active unit.

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[47] Chattaway, *J. Chem. Soc.*, **93**, 852 (1908); **95**, 1065 (1909).

The hitherto unaccountable similarity in the behavior of various oxidants of widely divergent potentials toward hydrazine is now explained on the ground that they are either *mono-delectronators*, yielding ammonia as the only by-product of the reaction, or *di-delectronators*, yielding both ammonia and hydronitric acid.

Further applications of this idea are projected, particularly for the case of other oxidation-reduction reactions in the fields of inorganic and organic chemistry in which intermediate products are formed.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

MICELLES AND THE ACTIVITY COEFFICIENT IN ALKALI SILICATE SOLUTIONS

BY MERLE RANDALL AND JESSIE Y. CANN

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The theory of colloidal electrolytes as used by McBain[1] postulates the replacement of a simple ion formed by the dissociation of an electrolyte, by a heavily hydrated polyvalent micelle or ion "which carries the equivalent sum-total of electrical charges" of the ions which it replaces. This theory was carefully considered by McBain and Salmon,[2] and by McBain, Laing and Titley,[3] who determined the dew point lowering and freezing point lowering of soap solutions. And from their data, Randall, McBain and White[4] calculated the activity coefficients.

McBain and Salmon[2] predicted that solutions of sodium silicate and certain other salts of the heavy metals, as well as the soaps, would be found to contain varying quantities of micelles. Recently, Harman[5] has postulated on the basis of his freezing point measurements, the existence of micelles in concentrated sodium silicate solutions containing a large excess of silica.

Before considering the constitution of the alkali silicate solutions as determined by their colligative properties, we will examine the significance of the activity coefficient of a solution in which micelles may be formed.

The Activity Coefficient in Solutions Containing Micelles

The activity of a solute is the ratio of the escaping tendency, or fugacity, of that constituent of a solution divided by the escaping tendency of the constituent in some standard state which is arbitrarily chosen.[6] The escaping tendency is, of course, independent of any assumed constitution

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[1] (a) McBain, *Trans. Faraday Soc.*, **9**, 99 (1913); (b) *Kolloid Z.*, **12**, 256 (1913).

[2] McBain and Salmon, THIS JOURNAL, **42**, 426 (1920).

[3] McBain, Laing and Titley, *J. Chem. Soc.*, **115**, 1289 (1919).

[4] Randall, McBain and White, THIS JOURNAL, **48**, 2517 (1926).

[5] Harman, *J. Phys. Chem.*, **31**, 355 (1927).

[6] See Randall, *Trans. Faraday Soc.*, **23**, 498 (1927).