Experimental

The first extracts of the seeds of *C. spectabilis* were made by soaking them in 1.25% sulfuric acid. The filtrate was shaken with Lloyd's alkaloid reagent. The basic material was liberated from the reagent with 0.1 *N* sodium hydroxide. This solution was extracted with successive portions of chloroform. Opaque crystals remained upon evaporation of the solvent.

Later extracts were made by soaking the seeds in 5% ammonium hydroxide for forty-eight hours, and extracting the filtrate with successive portions of chloroform. The crystals obtained upon evaporation of the solvent were dissolved in 1:1 hydrochloric acid, the solution thus formed was made alkaline with ammonium hydroxide, and extracted as above. Further purification was by repeated recrystallization from chloroform or absolute alcohol. Crystals from the alcohol were transparent. Crude extracts equivalent to 0.4, 0.07 and 0.015% of the dry weights of the seeds, leaves and stems, respectively, of *C. spectabilis* were prepared.

The extracted substance is soluble in chloroform and alcohol, slightly soluble in ether and very slightly soluble in water.

The compound slowly decolorizes potassium permanganate, and gives a yellowish color with Fröhde's (sulfomolybdic acid) reagent. It yields a yellowish precipitate with picric acid, a reddish-brown precipitate with Wagner's iodide reagent, a white precipitate with Mayer's reagent and a yellowish-white precipitate with Sonnenschein's phosphomolybdic acid reagent. It forms precipitates with salts of the heavy metals. All the tests were characteristic of alkaloids.

Melting point determinations of the purified compound were between 196 and 197° (uncorr.).

Anal. Calcd. for $C_{16}H_{26}O_6N$: C, 58.51; H, 7.98; N, 4.27. Found: C, 57.97; H, 7.85; N, 4.15.[6] The molecular weight, by the above formula, is 328.3. The determination of the neutral equivalent indicated a molecular weight of 324.

Pharmacologically, it lowers the blood pressure in dogs, and decreases the rate and amplitude of terrapin heart *in situ*. This decrease was observed even when the vagus nerve was severed. The rate of contraction of isolated heart muscle strips from terrapin is stimulated immediately, followed by a decrease in rate and amplitude.

The same lesions were observed in experimental animals administered lethal doses when either the whole seeds or alkaloid *per se* was used. This would indicate that the alkaloid isolated is the toxic principle of this plant. The twenty-four-hour lethal dose for chickens is 65 mg./kg. live weight.

Summary

The initial isolation of a specific alkaloid from the genus *Crotalaria* is reported. This compound has been named *monocrotaline* and was isolated from *C. spectabilis* Roth.

The compound melts at 196–197°, and has been given the empirical formula $C_{16}H_{26}O_6N$, tentatively.

The identity of the compound as the toxic principle of *C. spectabilis* has been established.

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[6] The authors are indebted to Dr. H. G. Shaw for the combustion analysis.

GAINESVILLE, FLA. RECEIVED OCTOBER 25, 1935

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

Energy Levels in Electrochemistry

BY WILDER D. BANCROFT AND JAMES E. MAGOFFIN

When measured against any standard electrode the changes $Cu \rightleftharpoons Cu^{++}$ and $Fe^{++} \rightleftharpoons Fe^{+++}$ are practically reversible. The change $H_2 \rightleftharpoons 2H^+$ is practically reversible at platinum black; but may show a large difference at zinc or mercury because the rate of change of atomic hydrogen to molecular hydrogen is rapid at platinum and relatively slow at zinc or mercury. To pass from hydrogen ion to molecular hydrogen, the system may have to pass through a higher energy level than molecular hydrogen. Given a substance which can be reduced at a lower energy level than that of molecular hydrogen, and it will be reduced at a platinum cathode. If the required energy level is above the molecular hydrogen level and below the atomic hydrogen level which we get with a zinc or mercury cathode, the substance cannot be reduced at a platinum cathode but can be at a zinc or mercury cathode. If the required energy level is above that to be reached with a zinc or mercury cathode, the substance cannot be reduced electrolytically in aqueous solution. Nobody is surprised at not being able to reduce methyl alcohol to paraffin; but no explanation has ever been given why it is impossible to reduce aqueous sodium sulfate or dilute sulfuric acid to sodium sulfite or sulfurous acid. The facts were known to Faraday. We have sealed up a sodium sulfate solution with platinum and hydrogen for six months without anything being formed in that time that would decolorize potassium permanganate.

This is the more remarkable because sodium sulfate and sulfurous acid can easily be oxidized electrolytically and can also be reduced electrolytically under suitable conditions. The answer is that in trying to go electrolytically from sodium sulfate to sodium sulfite, the system must pass through an energy level which is higher than any one can get with nascent hydrogen at a mercury cathode. The same thing holds true for sulfuric acid with this exception that the energy hump disappears experimentally if the sulfuric acid solution is made concentrated enough or hot enough.

We electrolyzed a 25 *N* solution of sulfuric acid with a smooth platinum foil anode and a platinized wire cathode at 50, 80 and 130°. At 50° no reduction of the sulfuric acid took place and the reaction products were hydrogen and oxygen. At 80° hydrogen and hydrogen sulfide were formed at the cathode because the rate of reduction was so slow compared with that of sulfurous acid that the latter was reduced as fast as formed. At 130° hydrogen and sulfur were formed, showing that the rate of reduction of sulfuric acid is fast enough to build up an appreciable concentration of sulfurous acid which then reacted with hydrogen sulfide to form sulfur. With a plain platinum foil cathode reduction of the sulfuric acid was not accomplished until a temperature of 130° was reached, at which temperature the products were hydrogen and hydrogen sulfide when a zinc cathode was used, reduction was obtained at 100°, sulfur and hydrogen being the products. The fact that platinized platinum accomplishes the reduction at a lower temperature than plain platinum indicates that absorption and activation of the sulfuric acid are important factors in the lowering of the energy hump of sulfuric acid.

One may ask why the reverse reaction is not identical with the forward reaction except in sign. The answer is that electrolysis sets free or tends to set free ions. There is no direct decomposition of an ion, such as $SO_4^= = SO_3^= + O$ or $NO_3^- = NO_2^- + O$. The forward reaction in the oxidation of a sulfite may be written: $SO_3^= + O = SO_4^=$ and the reverse reaction may be written $SO_4^= + 2H = SO_3^= + H_2O$; but the two reactions are not the same and are possibly never the same when there is a change in the composition of the ion. This concept of an intermediate energy level which may be higher than that of nascent hydrogen is quite different from the assumptions made by Conant and Lutz[1] of a reversible electrolytic process and a practically irreversible nonelectrolytic one.

It is well known that among metallic oxides the higher ones are stronger oxidizing agents and are more acidic than the lower oxides. With oxygen in the complex anion, this is not always true. Sulfuric acid is an oxidizing agent only at high concentrations or high temperatures, as in the oxidation of naphthalene and even there a catalyst is a great help. Potassium chlorate and perchlorate are weaker oxidizing agents at moderate temperatures than potassium hypochlorite, because of the high intermediate energy levels that must be passed through.

By changing the catalytic surface it is possible to do almost anything with sodium nitrate and nitrite.[2] Nitrate and nitrite are reduced about equally readily at a smooth platinum or copper cathode. Nitrite is reduced more readily than nitrate at a platinized cathode, and nitrate than nitrite at a pulverulent copper or silver cathode. With boiling solutions sodium nitrate can be reduced very effectively to nitrite either at a mercury cathode or with sodium amalgam. Measurements of the cathode potentials showed that overvoltages were a minor factor and that the phenomenon was a function of the nature and structure of the cathode.

At 25° there is practically no reduction of sodium chlorate at a smooth platinum cathode. On the other hand, Gladstone and Tribe[3] found, nearly sixty years ago, that pulverulent platinum or copper, saturated with hydrogen, reduced sodium chlorate to chloride. This could not be a question of electromotive force and experiment showed that there was a specific catalytic effect due to the form of the metal. Decomposition voltage curves were determined for 25 and 80°. Even at 25° there is a marked break in the curve for platinized platinum at a voltage at which no break can be detected in the corresponding curve for smooth platinum. At 80° with the platinized cathode there is first a curve representing reduction of the chlorate. Suddenly the cathode goes apparently passive and the curve changes to that for the evolution of hydrogen. This is due to impoverishment of sodium chlorate in the pores of

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(1) Conant and Lutz, THIS JOURNAL, **45**, 1047 (1923).

(2) Müller, *Z. anorg. Chem.*, **26**, 1 (1901); *Z. Elektrochem.*, **9**, 955 (1903); **11**, 509 (1905); Boehringer and Sons, *ibid.*, **12**, 745 (1906); Bancroft and George, *Trans. Am. Electrochem. Soc.*, **57**, 400 (1930).

(3) Gladstone and Tribe, *J. Chem. Soc.*, **33**, 139 (1878).

the platinized cathode. The effect comes on later and is more marked at the higher temperature owing to the higher rate of diffusion. The cathode can also be made to stay active longer by rotating it, thus increasing the rate of diffusion. The effect of rotation was not so striking as we had hoped that it would be.

Chlorate is evidently adsorbed and activated more strongly by pulverulent platinum or copper than by the smooth metals. This adsorption and activation of sodium chlorate by copper accounts for the puzzling reduction of chlorate by hydrazine in presence of pulverulent copper. Hodgkinson[4] reports that hydrazine can be boiled with a solution of sodium or potassium chlorate without any reduction of the chlorate taking place. In the presence of tarnished copper, quantitative reduction is obtained, apparently at room temperature. Only traces of copper are corroded, so the action must be catalytic. This is in accord with the electrolytic results. The tarnished copper is reduced to pulverulent copper which adsorbs and activates the chlorate so that it is reduced by the hydrazine. It is not the dissolved cuprous salt which acts catalytically, because we have shown that ammoniacal cuprous sulfate will not reduce chlorate. It is essential to oxidize all the cuprous salt with air before testing for chloride, because it was found that some chlorate is reduced if the solution is acidified before all of the cuprous salt has been removed.

With perchlorates the energy level to which the system must be raised is evidently much higher than with chlorates because nobody has yet succeeded in reducing perchlorates electrolytically in neutral or alkaline solutions. Williams[5] has shown that sodium perchlorate can be reduced by boiling with titanous sulfate and sulfuric acid. Since boiling sulfuric acid, if sufficiently concentrated, will decompose perchlorates,[6] there should be no difficulty in reducing perchlorates electrolytically near the boiling point if the right concentration of sulfuric acid is taken.

Chilesotti[7] found that molybdic acid, MoO_3, is reduced more rapidly to Mo_2O_3 at a platinized cathode than at a smooth platinum cathode; but that the reduction goes farther at a smooth platinum cathode. The first stage must be due to adsorption and activation; but it should be shown that the second stage calls for a higher voltage. Tafel[8] showed that in a sulfuric acid solution caffeine is reduced more readily at a mercury cathode than at a lead cathode, while the reverse is true for succinimide. This reversal must be due to selective adsorption in one or the other case, perhaps in both cases.

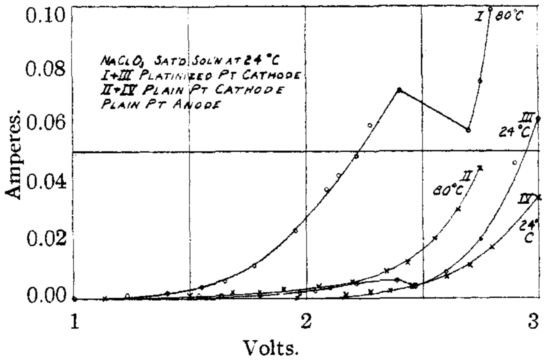

Fig. 1.

Conant and Cutter[9] have observed what appears to be a striking case of adsorption and activation. Dimethylacrylic acid is reduced by platinum and hydrogen but not by a chromous chloride solution, even though the latter is a stronger reducing agent than hydrogen by about 0.3 volt. Evidently the platinum activates the dimethylacrylic acid. If platinum is kept in a suitable chromous chloride or acetate solution until all the hydrogen is given off, that solution will undoubtedly reduce dimethylacrylic acid in presence of platinum. It is not yet necessary to differentiate in principle between hydrogenation and reduction.

People have become so used to speaking of electromotive forces of reversible reactions that most physical chemists believe that an irreversible reaction—assuming one to exist—cannot give a definite electromotive force. This is wrong. A given solution of sodium sulfite is at a definite energy level and changes to another energy level when it is oxidized to sodium sulfate. Since this reaction can be made to take place electrolytically under practically constant conditions, it must and does give a definite electromotive force.

If the sulfite–sulfate electrode were reversible, the limiting, ideal potential difference at a sulfite–sulfate electrode at constant *p*H would be given by the equation

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[4] Hodgkinson, *J. Soc. Chem. Ind.*, **33**, 815 (1914).

[5] Williams, *Chem. News*, **119**, 8 (1919).

[6] Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. II, 1922, p. 381.

[7] Chilesotti, *Z. Elektrochem.*, **12**, 146, 173, 197 (1906).

[8] Tafel, *Z. physik. Chem.*, **50**, 713 (1905).

[9] Conant and Cutter, THIS JOURNAL, **44**, 2651 (1922).

$$nFE = RT \ln \frac{P \cdot p_{SO_3}}{p_{SO_4}}$$

where p_{SO_3} and p_{SO_4} are the osmotic pressures of the sulfite and sulfate ions, respectively, and ln P is the Nernst integration constant. If the reaction is not reversible, the concentration of the sulfate ions has theoretically no effect, and the equation becomes

$$nFE = RT \ln P' \times p_{SO_3}$$

The same formula is obtained if the concentration of sulfuric acid is kept constant and this equation has been verified by Lewis, Randall and Bichowsky,[10] who did not know that the reaction was irreversible. They say that "equilibrium conditions apparently were not reached with great rapidity; but, upon standing, steady values were obtained reproducible to within about a millivolt."

"An iridized platinum electrode over which bubbled sulfur dioxide (diluted with air) was used in a solution of sulfuric acid. The other electrode was of mercury covered with mercurous sulfate in the same acid."

Their data are given in Table I.

TABLE I

ELECTROMOTIVE FORCE OF THE CELL $PtSO_2H_2SO_4$, $HgSO_4$-Hg AT 25°

Mol. % H_2SO_4	Pressure of SO_2 in atmospheres	E. m. f. volt	E. m. f. calcd. SO_2 1 atm. volt
0.09555	0.01328	0.301	0.356
.09555	.00689	.295	.358
.8946	.1091	.274	.302
.8946	.05080	.266	.305
.8946	.02479	.253	.306
.8946	.01328	.251	.306
.8946	.00689	.238	.302
.915	.969	.324	.324
.915	.969	.324	.324
4.618	.02489	.200	.247
4.618	.01333	.192	.247
10.303	.9814	.189	.189

In the cells in which the sulfuric acid concentration was kept constant at 0.8946 *M*, the equation describes with surprising accuracy the effect of changing the pressure of sulfur dioxide from 0.007 atm. to 0.109 atm., a ratio of more than fifteen to one. Increasing the concentration of the sulfuric acid decreases the electromotive force. We believe that this is not due to the change in the concentration of the sulfate ion, but to a change in the concentration of the hydrogen ion for which no term occurs in the equation. The experiment confirms the part of the theory which is right and disproves the parts that are wrong. Conant and Lutz[11] apparently obtained similar results for their irreversible reduction, though their wording is unnecessarily obscure.

We have confirmed the general results obtained by Lewis in our experiments on sodium sulfite, which of course gives a larger electromotive force against a calomel electrode than an equimolecular solution of sulfurous acid does. Some of our data are given in Table II. The calomel electrode is always cathode and no correction has been made for the liquid junction.

TABLE II

	Cell	E_c
1	Pt | *M*/10 Na_2SO_3 | Calomel	0.1308
2	Pt | *M* Na_2SO_3 | Calomel	.1455
3	Pt | *M* Na_2SO_3 + *M*/10Na_2SO_4 | Calomel	.1533
4	Pt | *M* Na_2SO_3 + *M* Na_2SO_4 | Calomel	.1488
5	Pt | *M* Na_2SO_3 + *M* NaCl | Calomel	.1816
6	Pt | *M* Na_2SO_3 + *M* NaBr | Calomel	.1878
7	Pt | *M* Na_2SO_3 + *M* NaCNS | Calomel	.2280
8	Pt | *M* Na_2SO_3 + *M* NaOH | Calomel	.2713
9	Pt | *M* Na_2SO_3 + *M* NaI | Calomel	.3015

Changing from tenth molar to molar sodium sulfite increases the observed electromotive force from 0.131 to 0.146, which is in the right direction. Adding sodium sulfate increases the electromotive force instead of decreasing it, as would be the case if the reaction were reversible. The fact that tenth molar sodium sulfate increases the electromotive force more, to 0.153, than does molar sodium sulfate, to 0.149, shows that at least two factors are at work. We have not yet tried to determine what the second one is. It was sufficient for the present to show that addition of the reaction product in considerable amounts did not lower the voltage. Addition of molar caustic soda raised the electromotive force from 0.156 to 0.271, which was in the direction to be expected.

Experiments with other salts were very interesting, as there is apparently a marked Hofmeister series, the electromotive force decreasing in the order: I > OH > CNS > Br > Cl > SO_4, with iodide coming above thiocyanate as it should do when adsorption is eliminated. The difference is very marked, E_c = 0.149 volt for sulfate and 0.302 volt for iodide. It is a question to what extent caustic soda owes its position to the *p*H or to displacing the water equilibrium. There are no facts which would have enabled us to predict that the electromotive force would be larger in iodide solutions rather than smaller.

One thing that must be done as soon as possible

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[10] Lewis, Randall and Bichowsky, THIS JOURNAL, **40**, 356 (1918).

[11] Conant and Lutz, *ibid.*, **46**, 1256 (1924).

is to devise methods for determining, at least approximately, the intermediate energy levels for sulfates, chlorates, perchlorates, etc. It should be clear that the difficulties that we have with these electrolytes are similar in principle to the difficulties that we have with organic compounds. Most of the passive resistances to change will prove to be energy humps.

Summary

The general results of this paper are:

1. The oxidation of dilute aqueous sulfurous acid or sodium sulfite is an irreversible reaction because, for reduction to take place, the system must pass through an energy level or energy hump which is higher than the energy level for nascent hydrogen as obtained by electrolysis.

2. With sulfuric acid solutions, and presumably with all other solutions, the energy hump decreases with increasing concentration, rising temperature and activating adsorption.

3. The stabilities of sodium chlorate and sodium perchlorate relatively to sodium hypochlorite are due to the intermediate energy levels which must be surmounted if reduction is to take place.

4. Sodium chlorate is adsorbed and activated so much by pulverulent copper that it can then be reduced by hydrazine.

5. An irreversible reaction may give a definite electromotive force. The limiting, ideal equation for the irreversible sulfite-sulfate electrode at constant pH is $nFE = RT \ln P' \times p_{SO_3}$.

6. All of Conant's work on irreversible reduction falls into line if one rejects the two assumptions of a reversible electrolytic step and a practically irreversible, non-electrolytic step. There is no experimental evidence for either, and both are superfluous. There is no reason at present for making any fundamental distinction between hydrogenation and reduction.

ITHACA, N. Y. RECEIVED AUGUST 27, 1935

[CONTRIBUTION FROM THE NATIONAL BUREAU OF STANDARDS, U. S. DEPARTMENT OF COMMERCE]

A Procedure for the Separation of the Six Platinum Metals from One Another and for their Gravimetric Determination[1,2]

BY RALEIGH GILCHRIST AND EDWARD WICHERS

In a paper[3] from this Laboratory, presented at the Ninth International Congress of Pure and Applied Chemistry in Madrid, April, 1934, a group of reactions was described which can be used for the quantitative separation of the six platinum metals from one another, and for their determination. The paper likewise contained a discussion of the analytical methods most generally used, and of certain others of special interest.

In this new system of analysis, the detailed procedure of which is given in the present paper, precipitation with ammonium chloride, fusion with pyrosulfate and extraction of metallic residues with acids are avoided entirely. The separation of platinum from palladium, rhodium and iridium is accomplished by controlled hydrolytic precipitation. When a boiling solution containing these four metals as chlorides, and in addition sodium bromate, is neutralized to approximately pH 7, the hydrated dioxides of palladium, rhodium and iridium precipitate quantitatively, leaving platinum in solution. A second precipitation of the dioxides suffices to effect complete removal of platinum. This method is applicable not only to the joint separation of palladium, rhodium and iridium from platinum, but also to the individual separation of these metals from platinum. It has a very great advantage over the older method by which platinum is separated from palladium, rhodium and iridium by precipitation with ammonium chloride. The hydrolytic method effects a clean separation of the platinum, whereas that in which the platinum is precipitated as ammonium chloroplatinate involves at least two inherent types of error. One type of error results from the persistent contamination of the platinum salt by rhodium and iridium (even though tervalent) and, to a less extent, by palladium. The other error occurs be-

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(1) Publication approved by the Director of the National Bureau of Standards of the U. S. Department of Commerce.

(2) Presented at the Meeting of the American Chemical Society in New York, April 25, 1935.

(3) R. Gilchrist and E. Wichers, "A New System of Analytical Chemistry for the Platinum Metals." Paper No. 178 of the Scientific Program of the Ninth International Congress of Pure and Applied Chemistry. As the proceedings of the Congress have not been published, reprints of this paper are not yet available.