The value of this potential at 0° was found to be **1.601** volts (in 1.0 *f* HNO_3).

It is interesting to note that in sulfate solution Kunz[6] obtained much smaller values, namely, 1.461 and 1.443 volts at 25° in 0.5 *f* and in 1.0 *f* H_2SO_4, respectively. This indicates that complex formation between the ceric ion and sulfate ion (or hydrosulfate ion) takes place to a large extent. It is probable therefore that the value obtained in nitric acid represents much more nearly the *molal* oxidation potential of cerous–ceric *ions*.

It may also be noted that the cerous–ceric potential in nitrate solution is of the same order as that (1.59 volts)[11] for the reaction $MnO_4^- + 4H^+ + 3E^- = MnO_2(s) + 2H_2O(l)$. Correspondingly, on adding permanganate solution to a nitric acid solution of cerous nitrate, manganese dioxide was found to form; and on adding ceric nitrate solution to freshly precipitated manganese dioxide, the color of permanganate was developed.

[11] Brown and Tefft, THIS JOURNAL, **48**, 1128 (1926).

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Strong Oxidizing Agents in Nitric Acid Solution. II. Oxidation Potential of Thallous-Thallic Salts

BY ARTHUR A. NOYES AND CLIFFORD S. GARNER

Previous and Proposed Investigations

The thallous–thallic oxidation potential has been studied by several investigators. Its determination was first undertaken by Spencer and Abegg[1] who studied the potential in nitric, hydrochloric and sulfuric acids, and in the presence of various salts with the view of investigating complex-ion formation. Their measurements were made at 25° against a 0.1 *N* calomel half-cell as a reference electrode, and their potentials were not corrected for liquid-junction potentials. Grubb and Hermann[2] later obtained values for the thallous–thallic potential in sulfuric acid solutions. Measurements by them were made at 18° against either a normal calomel electrode or a mercurous sulfate electrode, and liquid-junction corrections were not applied. Partington and Stonehill[3] recently measured at 25° cells of two types

$$\mathrm{Pt}, \left\{ H_2SO_4\,(c) + \begin{matrix} Tl_2SO_4\,(c_1) \\ Tl_2(SO_4)_3\,(c_2) \end{matrix} \right\}, H_2SO_4\,(c), H_2\,(1\ \mathrm{atm.}) + \mathrm{Pt}$$

and

$$\mathrm{Pt}, \left\{ H_2SO_4\,(c) + \begin{matrix} Tl_2SO_4\,(c_1) \\ Tl_2(SO_4)_3\,(c_2) \end{matrix} \right\}, Hg_2SO_4\,(\mathrm{satd.}), Hg, Hg_2SO_4\,(\mathrm{satd.}), H_2SO_4\,(c), H_2(1\ \mathrm{atm.}) + \mathrm{Pt}$$

These investigations showed that the oxidation potential of thallous–thallic salts varies greatly with the nature of the anion present, doubtless owing to the formation of anion complexes; and as these complexes are probably produced in minimum quantity with monobasic oxyacids, such as nitric acid and perchloric acid, thereby yielding a molal potential approximating most closely that of the simple thallous and thallic ions, we have measured and describe in this paper cells of the type

$$\mathrm{Pt} + H_2\,(1\ \mathrm{atm.}), HClO_4\,(c'), \left\{ HNO_3\,(c) + \begin{matrix} Tl^{III}\,(c_2) \\ Tl^{I}\,(c_1) \end{matrix} \right\}, \mathrm{Pt}$$

During the progress of our investigation an article upon the thallous–thallic potential in perchloric acid solution has been published by Sherrill and Haas,[4] thereby making possible a comparison of the potential in the two monobasic oxyacids.

Apparatus and Materials

Preparation and Analysis of the Solutions.—A weighed quantity of C. P. thallous nitrate, dried in an oven at 140°, was dissolved in a definite weight of distilled water, and the resulting solution was divided into two nearly equal portions.

(1) From one of these portions a thallic nitrate solution was prepared by oxidation with a gas mixture containing 5% by volume of ozone (Noyes, Hoard and Pitzer[5]), thereby avoiding the introduction of foreign substances into the solution. To it had previously been added the amount of strong nitric acid (freed from nitrogen dioxide by bubbling air through it) required to leave the oxidized solution 0.5 *f* in nitric acid. It was thought that this acid would suffice to prevent the hydrolysis of the thallic nitrate formed, but during the oxidation dark-brown thallic hydroxide precipitated, and it was necessary to add more nitric acid to the oxidized mixture. The excess of ozone was blown out with oxygen, and the thallic nitrate solution was analyzed in the following way.

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[1] Spencer and Abegg, *Z. anorg. Chem.*, **44**, 379 (1905).

[2] Grubb and Hermann, *Z. Elektrochem.*, **26**, 291 (1920).

[3] Partington and Stonehill, *Trans. Faraday Soc.*, **31**, 1357 (1935).

[4] Sherrill and Haas, THIS JOURNAL, **58**, 952 (1936).

[5] Noyes, Hoard and Pitzer, *ibid.*, **57**, 1223 (1935)

TABLE I

OBSERVED AND COMPUTED ELECTROMOTIVE FORCES AT 25 AND 0°

Temp., °C.	HNO_3 c	$HClO_4$ c'	$TlNO_3$ c_1	$Tl(NO_3)_3$ c_2	Tl^I/Tl^{III} c_1/c_2	Mean ionic strength, μ	$E_{obsd.}$	E_C	E_L	E_H	E^0
25	2.000	2.000	0.07264	0.04720	1.5392	2.17	1.2096	+0.0055	−0.0096	+0.0244	1.2299
	(α, 0.759)	(α', 1.295)	.06499	.05819	1.1194		1.2138	+ .0014	− .0096	+ .0244	1.2300
										Mean	1.2300
25	1.000	1.000	.04999	.00406	12.314	1.09	1.2048	+ .0323	− .0023	− .0056	1.2292
	(α, 0.706)	(α', 0.803)	.04133	.01643	2.5148		1.2273	+ .0119	− .0023	− .0056	1.2313
			.03574	.02445	1.4617		1.2346	+ .0049	− .0023	− .0056	1.2316
			.02874	.03442	0.8351		1.2407	− .0023	− .0023	− .0056	1.2305
			.02146	.04484	0.4786		1.2489	− .0095	− .0023	− .0056	1.2315
			.00514	.06817	0.0754		1.2708	− .0332	− .0023	− .0056	1.2297
										Mean	1.2306
25	0.5000	1.000	.01624	.01455	1.1155	0.55	1.2499	+ .0014	− .0147	− .0056	1.2310
	(α, 0.708)	(α', 0.803)	.00691	.02788	0.2479		1.2677	− .0179	− .0147	− .0056	1.2295
										Mean	1.2303
										General Mean	**1.2303**
0	1.000	1.000	.02874	.03442	0.8351	1.09	1.203	− .0021	− .0021	− .0051	**1.193**
	(α, 0.706)	(α', 0.803)									

To a weighed sample solid potassium chloride and mercury were added, the mixture was shaken for two minutes and filtered through a Jena glass filter. The filtrate with washings was then titrated with standard sodium hydroxide solution to determine the nitric acid content. It was necessary to reduce the thallic salt in this way, since otherwise it separated out as the hydroxide and obscured the end-point. The content in thallic nitrate was determined on separate samples by reducing the thallic thallium to thallous thallium with sulfur dioxide, blowing out the excess of sulfur dioxide with carbon dioxide, and determining the thallium by two independent methods. However, it was found that the large amount of nitrate present interfered with these determinations; so the samples were first fumed with concentrated sulfuric acid to convert the nitrate to sulfate. Two determinations were made by the iodate method using the iodine monochloride end-point,[6] and these agreed to better than 0.1% with two determinations by the bromate method using methyl orange as an oxidation indicator.[7] The absence of thallous thallium in the thallic nitrate solution was proved by making a sample 5 *f* in hydrochloric acid, adding a small amount of iodine monochloride solution and shaking with carbon tetrachloride; no iodine color was perceptible. The thallic nitrate stock solution thus prepared was 0.1835 *f* in thallic nitrate and 2.430 *f* in nitric acid.

(2) To the other portion of the thallous nitrate solution was added enough nitric acid to make the resulting solution of the same acidity as the thallic nitrate stock solution. Analyses for both thallium and acid checked the values obtained by the direct synthesis of the solution. The thallous nitrate stock solution was 0.1284 *f* in thallous nitrate and 2.430 *f* in nitric acid.

The Electrolytic Cell.—The electrolytic cell used for the electromotive force measurements was that described in the preceding paper. The platinum wire electrode gave the same potential whether it was bright or platinum-blacked; however, equilibrium was more rapidly attained in the latter case.

Method of Potential Measurements.—The equipment used and the method of making the electromotive force measurements were those previously described in detail. The potential of a given cell was observed over a period of one to seventy hours. Equilibrium was reached within an hour, and subsequent readings were constant to 0.1 mv., stirring having no effect on the potential.

Measurements at 0°. One of the cells which had been measured at 25° was transferred to a 0° thermostat, and its potential observed over a period of three days. Equilibrium was much more slowly attained than at 25°, and the readings were sensitive only to about 0.5 mv. The cell was afterward returned to the 25° thermostat, and gave substantially the same electromotive force as before. The probable error of the formal potential at 0° is about one millivolt.

The Observed and Computed Electromotive Forces

In Table I are shown the concentration data, the observed electromotive forces, $E_{obsd.}$, the corrections applied to these, and the computed formal oxidation potentials E^0 resulting thereby, all in just the same form in which these quantities are presented in Table I of the preceding article. The activity coefficients α and α' of the two acids are as before taken from the data of Pearce and Nelson[8] and of Abel, Redlich and v. Lengyel,[9] the same values being used at 0° (where data are lacking) as at 25°.

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[6] Swift and Garner, THIS JOURNAL, **58**, 113 (1936).

[7] Kolthoff, *Rec. trav. chim.*, **41**, 172 (1932); Zintl and Rienäcker, *Z. anorg. allgem. Chem.*, **153**, 278 (1926); see also Noyes, Pitzer and Dunn, THIS JOURNAL, **57**, 1231 (1935).

[8] Pearce and Nelson, *ibid.*, **55**, 3080 (1933).

[9] Abel, Redlich and v. Lengyel, *Z. physik. Chem.*, **132**, 204 (1928).

Summary and Discussion

Measurements have been described above of the electromotive forces at 25 and 0° of cells of the type

$$\mathrm{Pt} + \mathrm{H_2}\,(1\ \mathrm{atm.}),\ \mathrm{HClO_4}\,(c'),\ \left\{ \mathrm{HNO_3}\,(c) + \frac{\mathrm{Tl^{III}}\,(c_2)}{\mathrm{Tl^{I}}\,(c_1)} \right\},\ \mathrm{Pt}$$

From these measurements presented in Table I the formal oxidation potential E^0 of the reaction $\mathrm{Tl^{III}} + 2\mathrm{E^{-I}} = \mathrm{Tl^{I}}$ has been computed to have the value **1.2303** ± 0.0007 volt at 25° and the value **1.193** ± 0.001 volt at 0° in nitric acid solution. This value is shown to remain substantially constant when the ratio $\mathrm{Tl^I/Tl^{III}}$ is varied one hundred-fold and when the concentration of nitric acid is varied from 0.5 to 2 *f*. This constancy of the potential shows that neither hydrolysis of the thallic nitrate (by a reaction like $\mathrm{Tl^{+++}} + \mathrm{H_2O} = \mathrm{TlOH^{++}} + \mathrm{H^+}$), nor formation of nitrate complexes occurs to a considerable extent with thallic salts in nitric acid solutions between 0.5 and 2.0 formal.

This value, 1.230 volts, of the formal potential is slightly lower than those found by Sherrill and Haas[4] for the thallous–thallic potential in perchloric acid solution, who obtained at 25° 1.260 volts for the formal potential in 1.0 *f* perchloric acid and 1.247 volts for the extrapolated molal potential for thallous–thallic ions.

Noteworthy is the fact that the thallous–thallic potential in sulfuric acid solution, determined by Partington and Stonehill[3] to be 1.20 to 1.22 volts, is of about the same magnitude as the potentials in nitric and perchloric acids indicating that the formation of sulfate complexes by thallic sulfate is not very extensive.

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The Electron Diffraction Study of Paraldehyde

BY D. C. CARPENTER AND L. O. BROCKWAY

Paraldehyde has been shown[2] to exist as the trimer $(\mathrm{CH_3CHO})_3$ in the gaseous state and in solution in phenol, and metaldehyde as the tetramer $(\mathrm{CH_3CHO})_4$ in phenol solution. In the present work the configuration of paraldehyde has been established by electron diffraction methods as a staggered six-membered ring of alternate carbon and oxygen atoms with a hydrogen atom and a methyl group attached to each of the ring carbon atoms, the methyl carbon atoms being approximately coplanar with the ring oxygen. The technique of the electron diffraction method of determining the structure of molecules has been described,[3] and the method now represents one of the most direct and feasible means of determining bond angles and distances.

Experimental

The sample of paraldehyde used in this study was purified by repeated fractional distillation and boiled at 124.0 ± 0.2°. Smits and deLeeuw[4] record the boiling point as 123.7°.

The low vapor pressure of paraldehyde at room temperature prevented the use of the ordinary unheated gas nozzle. In this investigation the sample was placed in a small glass bulb which was sealed to a copper tube leading through an all-metal high vacuum valve and up into the apparatus where it terminated in a nozzle just below the electron beam. The sample bulb, connecting tubes, valve and nozzle were all heated by spirals of resistance wire enclosing the entire path of the vapor. The valve was constructed so that a stiff spring pressing on the valve stem compensated for relative expansion of the valve parts and the valve was vacuum tight both at ordinary and elevated temperatures. Four thermocouples were used to follow the temperatures of the various parts of the assembly. This arrangement for handling vapors at high temperatures differs from those used by other investigators in which the gas stream flows continuously and is regulated by changes of the temperature of the sample holder. Here the gas flow is controlled by a quick-acting valve.

Fifteen photographs of paraldehyde were obtained in three sets with the temperature of the sample ranging from 103 to 115°. The exposure

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(2) W. Burstyn, *Sitzber. Wiener Akad.*, **511** (1902).

(3) L. Pauling and L. O. Brockway, *J. Chem. Phys.*, **2**, 867 (1934).

(4) A. Smits and H. L. deLeeuw, *Z. physik. Chem.*, **77**, 269 (1911).