THE OXIDATION OF MERCURY BY NITRIC ACID

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November 30, 1957

AEC RESEARCH AND DEVELOPMENT REPORT

PHILLIPS PETROLEUM CO.
ATOMIC ENERGY DIVISION
(UNDER CONTRACT NO. AT (10-1)-205)
IDAHO OPERATIONS OFFICE
U.S. ATOMIC ENERGY COMMISSION

PRICE 75¢

Available from the
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Under Contract
AT(10-1) -205

Idaho Operations Office
U. S. Atomic Energy Commission

* A portion of this report was submitted by R. F. Murray in partial fulfillment of the Masters of Science Degree at the University of Idaho.

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THE OXIDATION OF MERCURY BY NITRIC ACID

I. Summary

The oxidation of mercury in nitric acid has been investigated. An empirical rate law, oxidation rates and mercury species in solution have been determined. A reaction mechanism based on the presence of nitrous acid can be interpreted in terms of the rate expression derived.

II. Introduction

Study of the mechanism of the mercury-catalyzed nitric acid dissolution of aluminum-uranium alloy fuel elements has led to the conclusion that mercury is formed on the aluminum oxide surface during dissolution. The mercuric ion-mercury Redox cycle acts as an intermediate step in the overall aluminum reaction with nitric acid. The protective oxide coating on the aluminum presents to the dissolving medium a negatively-charged surface tightly bound to the metal by the space charge existing across the semi-conductor oxide layer. The cations in the dissolving agent will be attracted to the negatively charged surface in preference to the anion. The mercuric and hydrogen ions are available to react. Two factors, the easy polarizability of mercuric ion and the hydrogen overvoltage requirements, result in the formation of mercury as the main surface reaction. Then the mercury is readily reoxidized in the nitric acid medium thereby keeping the Redox cycle in operation.

This study was initiated to better understand the reactions between mercury and nitric acid. Oxidation rates, empirical rate laws and the mercury species existing in solution have been determined.

III. Discussion of Mechanism and Rate Law

The necessity for the presence of nitrous acid in nitric acid to oxidize mercury has been reported in Bancroft (1), Klemenc (2), Yost and Russel (3). The exact path by which this reaction proceeds is in dispute. Bancroft holds that HNO_2 activates the HNO_3 through the dynamic equilibrium $\text{HNO}_3 + \text{HNO}_2 = 2\text{NO}_2 + \text{H}_2\text{O}$. Klemenc proposes the formation of an intermediate known as E^- - acid. Another path is that proposed in Yost and Russel in describing the decomposition of nitrous acid according to Abel. Since the primary objective of this study was to determine the factors affecting the rate of oxidation of mercury and their relative significance rather than to determine the exact mechanism of oxidation, it will suffice to consider the oxidation of mercury to occur directly through nitrous acid, neglecting intermediate or secondary reactions.

Latimer (4) lists the following potential data for the oxidation of Hg to Hg_2^{++} and Hg^{++} .

These data show that mercury is a weak reducing agent. The choice of a path for the reduction of nitrous acid by mercury should therefore be limited to one involving a single electron change. That is, the reduction of the nitrogen in the nitrous acid would not be expected to go to a lower oxidation state than plus two. The reaction,

involves only a one electron change and exhibits a favorable redox potential with mercury. Furthermore, the product, nitric oxide, is quite stable and further reduction usually requires a reducing agent that is electropositive.

Based on the same reasoning, the direct oxidation of Hg to Hg^{++} involving a single two electron change need not be considered. The remaining possibility of a three body collision involving two single electron changes is far less probable than the stepwise oxidation and ratewise would not be expected to be significant.

On these bases, the following reactions can be postulated for the oxidation of mercury.

It is also known that in the presence of metallic mercury, ionic species of mercury react as follows:

The equilibrium constant for this reaction at 25°C is given by Latimer (4) as,

$$K = \frac{k_3}{k_{-3}} = 166$$

Since nitrous acid is involved in Reactions (1) and (2), its origin must be considered. Sufficient nitrous acid is present as an impurity in nitric acid to initiate the mercury oxidation. Once the mercury dissolution is underway nitric oxide is formed and it is possible to form a greater concentration of nitrous acid through the following

Reaction (4) has a positive free energy at standard conditions but the reaction is reversible and it is still possible to form appreciable amounts of N_2O_4 . However, reactions (5) and (6) are rapid in comparison to (4) so that any N_2O_4 formed would be depleted immediately. Therefore, reactions (4), (5), and (6) can be combined to eliminate N_2O_4 giving the following single reaction:

In summary, the mercury oxidation can be described by the series of reactions (1), (2), (3), and (7) which are:

The simplest approach to postulation of a rate law is to determine the overall significance of the various components in the above series of reactions by summation. Thus the overall reaction can be represented by the following generalized expression:

A rate law based on this generalized expression will take the following form:

$$-\frac{d(Hg)}{dt} = k_f (\text{metal surface area})^i (H^+)^j (NO_3^-)^k (HNO_2)^l \quad (9)$$

neglecting the effect of reaction products and the reverse reaction. Simplification of the rate law can be accomplished by considering the fate of the nitrous acid in the reaction.

Rate coefficients for reaction (7) were determined in studies of the decomposition of nitrous acid. According to Yost (3), Abel, Bray and others found the following values:

$$-\frac{d(HNO_2)}{dt} = \frac{k_7 (HNO_2)^4}{p_{NO}^2}$$

$k_7 = 46 \text{ at } 25^\circ\text{C}$
 $= 5130 \text{ at } 60^\circ\text{C}$
 $= 50000 \text{ at } 90^\circ\text{C} - \text{Extrapolated}$
 $\text{from Abel's data in moles, liters, minutes, atmospheres.}$

$\left. \begin{array}{l} \text{Abel's data} \\ \text{(10)} \end{array} \right\}$

For the reverse reaction:

$$\frac{d(\text{HNO}_2)}{dt} = k_8 (\text{HNO}_2) (\text{H}^+) (\text{NO}_3^-) \quad k_8 = 1.6 \text{ at } 25^\circ \quad (11)$$

At equilibrium $\frac{d(\text{HNO}_2)}{dt} = 0$

$$\text{and } K = \frac{k_7}{k_8} = \frac{(\text{H}^+) (\text{NO}_3^-)}{(\text{HNO}_2)^3 P_{\text{NO}}}^2 \quad (12)$$

$$\begin{aligned} K &= 28.7 \text{ at } 25^\circ\text{C} \\ &= 39.6 \text{ at } 30^\circ\text{C} \end{aligned} \quad \text{Abel's data}$$

$$= 1900 \text{ at } 90^\circ\text{C} \quad \text{Extrapolated from Abel's data}$$

This equilibrium at one atmosphere NO pressure takes the form,

$$(\text{HNO}_2)^3 = \frac{(\text{H}^+) (\text{NO}_3^-)}{K} \quad (13)$$

On the basis of these data and general rate laws for reactions (1), (2), and (3), the rate of change of nitrous acid can be expressed in the following manner assuming the partial pressure of nitric oxide is one atmosphere:

$$\begin{aligned} \frac{d(\text{HNO}_2)}{dt} &= k_8 (\text{HNO}_2) (\text{H}^+) (\text{NO}_3^-) - k_7 (\text{HNO}_2)^4 - k_1 (\text{HNO}_2)^m (\text{H}^+)^n (\text{Area})^p \\ &\quad - k_2 (\text{HNO}_2)^q (\text{H}^+)^r (\text{Hg}_2^{++})^s \end{aligned} \quad (14)$$

Certain deductions can be made from this expression and a knowledge of the rate constants k_7 and k_8 . By extrapolation of Abel's data to 90°C , values for k_7 and k_8 of approximately 50000 and 25 respectively were determined. Again assuming sufficient nitrous acid to be present as an original impurity in nitric acid (say 10^{-6} - 10^{-5} molar), oxidation of mercury would be initiated. Since nitrous acid is regenerated in the process through nitric oxide by reaction (7) the concentration of nitrous acid would rise. When the partial pressure of nitric oxide reaches 1 atmosphere expression (14) applies. Substituting the appropriate values of k_7 and k_8 yields,

$$\begin{aligned} \frac{d(\text{HNO}_2)}{dt} &= 25 (\text{HNO}_2) (\text{H}^+) (\text{NO}_3^-) - 50000 (\text{HNO}_2)^4 - k_1 (\text{HNO}_2)^m (\text{H}^+)^n (\text{Area})^p \\ &\quad - k_2 (\text{HNO}_2)^q (\text{H}^+)^r (\text{Hg}_2^{++})^s \end{aligned} \quad (15)$$

From (15) it should be evident that for any given appreciable concentration of nitric acid and very low concentrations of nitrous acid that $d(\text{HNO}_2)/dt$ would be positive even for appreciable rates of mercury oxidation; i.e., the concentration of nitrous acid would be increasing. However, a limiting concentration of nitrous acid is approached as the positive and negative terms of equation (15) approach equality and the rate becomes zero. According to equation (15) the limiting concentration of nitrous acid is less than one molar.

When $\frac{d(\text{HNO}_2)}{dt} = 0$

$$k_8 (\text{HNO}_2) (\text{H}^+) (\text{NO}_2^-) = k_7 (\text{HNO}_2)^4 + k_1 (\text{HNO}_2)^m (\text{H}^+)^n (\text{Area})^p + k_2 (\text{HNO}_2)^q (\text{H}^+)^r (\text{Hg}_2^{++})^s \quad (16)$$

To gain further insight into the relationships of the species in equation (16), assume m, n, q, and r equal one, then

$$k_7 (\text{HNO}_2)^3 = (\text{H}^+) \left[k_8 (\text{NO}_3^-) - k_1 (\text{Area})^p - k_2 (\text{Hg}_2^{++})^s \right] \quad (17)$$

The basis for simplification of the rate law afforded by equation (16) and simplified in equation (17) is that it shows the concentration of nitrous acid is a function of nitric acid concentration, the metal surface area, and the concentration of Hg_2^{++} .

The HNO_2 term is therefore a function of the other terms already appearing in the generalized rate law describing the disappearance of mercury with the exception of the mercurous ion which was omitted because its effect on the forward rate was unknown. It can now be established from equation (17) that this term would be negligible if $k_2 \ll k_8$ or if the mercurous ion concentration is small compared with the nitric acid. So the rate law to be investigated can be written as,

$$\frac{-d(\text{Hg})}{dt} = k(\text{area})^x (\text{H}^+)^y (\text{NO}_3^-)^k \quad (18)$$

IV. Measurement of Rate of Mercury Dissolution

Mercury dissolution experiments were performed in a two-liter pyrex glass resin reaction flask. This was equipped with a condenser, stirrer, and glass cooling coil and a glass-coil heater as shown in Figure 1. It was possible to control the reaction temperature within $\pm 0.5^\circ\text{C}$ by using a glass-enclosed mercury thermoregulator. The temperature control was adequate for the expected low value of the activation energy and the temperature involved. It was found that cooling the solution only kept the temperature within the proper temperature limits in the mercury. To keep a constant area mercury surface exposed at all times, a shallow dish with vertical sides was placed in the bottom of the reaction vessel and the mercury placed inside the dish.

In all the experiments the nitric acid was heated to the proper temperature and then distilled mercury was added to the reaction vessel. The stirrer was not operated for the first two minutes of the reaction. This gave the reaction products an opportunity to build up sufficient concentration to sustain the reaction.

Samples were removed during the runs and analyzed for hydrogen ion, mercurous ion, and total mercury in solution.

Figure 1

MERCURY DISSOLUTION APPARATUS

Acid was determined by potentiometric titration with sodium hydroxide to a pH of 5.50. An eight percent solution of potassium oxalate in saturated potassium chloride was added to overcome any bias caused by the ionic mercury species present. Mercurous ion was precipitated as mercurous chloride and weighed to determine the concentration. Two methods were utilized to determine total mercury (or Mercury II). By the first method, the filtrate from the chloride precipitation for mercurous mercury was titrated potentiometrically with silver nitrate to determine the excess chloride. The mercuric ion was determined by the difference in the chloride precipitated as mercurous chloride and that precipitated as silver chloride. By method two, the total mercury was determined by first oxidizing all the ionic mercury species present to the plus two valence state with ceric ion. Then a thiocyanate titrimetric determination was made. Mercury II was found by the difference between total mercury and mercury I. The results of the dissolution experiments are listed in Table IV.

Table I is a summary of the experimental conditions.

TABLE I
List of Experiments
Temperature 90°C.

<u>Run</u>	<u>HNO₃M</u>	<u>Area, cm²</u>
1	4.0	79.8
2	4.0	79.8
3	4.0	79.8
4	5.5	79.8
5	5.5	79.8
6	2.0	79.8
7	2.0	79.8
8	4.0	42.8

In Runs 1 and 2, the total mercury was determined by the chloride method described in the analytical procedures. In all other experiments, the thiocyanate titration method was used to determine total mercury.

Nitrate concentration was calculated by equating it with the total cation concentration. In runs where the values were very erratic, (NO₃⁻) was determined as a function of (H⁺) for purposes of determine k.

V. Results

Stoichiometric data are summarized in Table II. The experimental data indicate the reactants have the following most reasonable, stoichiometric relationship.

The equations originally proposed for consideration as possible mechanism can now be combined in a suitable form to fit the stoichiometry of the reactants.

However, the uncertainty indicated in the tables makes it obvious that the stoichiometry is only approximate and that the above relationships change slightly during the course of dissolution.

TABLE II

Stoichiometry of Mercury Dissolution in Nitric Acid at 90°C

Initial Nitric Acid Conc., <u>M</u>	Moles Acid Consumed Per Mole of Nitrate		Moles Acid Consumed Per Mole of Mercury	
	Ratio, H^+/NO_3	Precision, $\alpha^* = 0.05$	Ratio, H^+/Hg	Precision $\alpha = 0.05$
2.0	4.74	+ 1.89	1.49	+ 0.08
4.0	3.75	+ 0.38	1.81	+ 0.78
5.5	4.05	+ 2.04	1.74	+ 1.22

* = The level of probability at which the precision estimate is made.

Testing of the experimental data showed that a plot of the logarithm of acid concentration against time resulted in a straight line. From this, one may conclude either:

1. Hydrogen ion appears to the first power in the rate expression and nitrate and mercury are to the zero power.
2. The reaction is pseudo-first order in hydrogen ion because the nitrate ion is considered constant. Mercury is assumed zero order because it is an area function and does not affect the initial conditions in any other way.

With respect to the first condition, the half-life of a true first order reaction is not dependent on initial conditions but only on the reaction constant.

$$t_{1/2} = \frac{\ln 2}{k}$$

The half-lives in the experiments show a variation with initial conditions so the first proposition must be excluded. Examination of the second possibility in light of this information indicates the nitrate must appear as a higher power function than zero. Assuming the mercury is zero order in the rate law and treating nitrate as constant gives from the stoichiometry:

The relation:

$$-\frac{d(\text{Hg})}{5 dt} = -\frac{1}{8} \frac{d(\text{H}^+)}{dt} = -\frac{1}{2} \frac{d(\text{NO}_3^-)}{dt} = k (\text{area}) (\text{H}^+) (\text{NO}_3^-)_o^n \quad (20)$$

or simply:

$$-\frac{d(\text{H}^+)}{dt} = 8 k (\text{area}) (\text{H}^+) (\text{NO}_3^-)_o^n \quad (21)$$

which integrated is:

$$\ln (\text{H}^+_o) = 8 k (\text{area}) (\text{NO}_3^-)_o^n t \quad (22)$$

(Subscript o refers to initial conditions)

Then for the half-life:

$$t_{1/2} = \frac{\ln 2}{8 k(\text{area}) \text{NO}_3^-)^n} \quad (23)$$

Now it is possible to find the approximate value of n by comparing initial conditions and half-lives, the other terms in the expression being constant. So:

$$\frac{t_{1/2a}}{t_{1/2b}} = \left(\frac{(\text{NO}_3^-)_{ob}}{(\text{NO}_3^-)_{oa}} \right)^n \quad (24)$$

Values of the half-lives are given in Table III.

TABLE III

Half Lives of Acid (H^+)

<u>Initial Nitric Acid Acid Conc., M</u>	<u>Half-life, Minutes</u>
5.51	6.1
4.04	13.2
1.98	74.8

For the half-life calculation in the integrated form, treating the rate as first order:

$$k = \frac{\ln 2}{(8) (\text{area}) (t_{1/2})} \quad (25)$$

The expression is modified for an overall k^* involving $(\text{NO}_3^-)^n$

$$k^* = \frac{\ln 2}{(8) (\text{area}) (t_{1/2}) (\text{NO}_3^-)^n} \quad (26)$$

Then the two k values are related by this equation

$$k = k^* (\text{NO}_3^-)^n \quad (27)$$

First the values of k were calculated for each experimental point; then the overall k^* and n were determined by the method of least squares. The expression relating the values of k and k^* to which the method of least squares was applied took the form:

$$\log k = \log k^* + n \log (\text{NO}_3^-) \quad (28)$$

The values for k^* and n obtained in this way are:

$$k^* = 2.32 \times 10^{-6} \text{ liters } 2.86 \text{ moles }^{-2.86} \text{ cm}^{-2} \text{ min}^{-1}$$

$$n = 2.86 \pm 0.24$$

Much of the uncertainty can be associated with the method of determination of the nitrate ion concentration. At the time of the experiments it was not possible to evaluate the nitrite species present or off-gas composition. As previously mentioned, until one can evaluate the true significance of the (NO_3^-) term in relation to all the nitrogen oxygen species present, the approach used must suffice.

To test the rate law, average values of acid and nitrate for the various times were determined from the experimental points. Values of ΔH^+ were then determined and Δt was calculated by using the rate equation,

$$-\frac{1}{8} \frac{d(\text{H}^+)}{dt} = 2.32 \times 10^{-6} (\text{area}) (\text{H}^+) (\text{NO}_3^-)^{2.86 \pm 0.24} \quad (29)$$

The calculated values of equation (29) are shown as the curves in Figures 2 to 4. The (NO_3^-) value during the course of a run was determined as a function of acid concentration from stoichiometry. The uncertainty in the calculated value indicated arises from the uncertainty in the stoichiometry.

The proposed rate law does agree reasonably well with mean calculated values and is satisfactory for the purpose intended. The original assumptions concerning nitrous acid appear adequate.

By relation (20) the rate of appearance of total ionic mercury was determined from the calculated rate of disappearance of acid. These data are also plotted in Figures 5 to 7 and compared with experimental data. As might be expected in view of the application of an average stoichiometric ratio, the agreement between experimental and calculated data is not as good as that obtained for acid.

VI. Summary

The rate of dissolution of mercury metal in 2.0, 4.0, and 5.5 molar nitric acid was studied. An empirical rate law,

$$-\frac{1}{8} \frac{d(\text{H})}{dt} = \frac{1}{5} \frac{d(\text{Hg})}{dt} = 2.32 \times 10^{-6} (\text{area}) (\text{H}^+) (\text{NO}_3^-)^{2.86 \pm 0.24}$$

(At 90°C, 1 atmosphere pressure and 1 liter solution volume) was found to agree reasonably well with experimental data. This law is based on the average stoichiometry:

which can be related to the following mechanism:

From the experimental data available it is not feasible to correlate the mechanism in a manner that is exactly consistent with the experimental rate law. Further refinement would require experimental evaluation of the factors controlling nitrous acid concentration.

VII. Acknowledgements

The authors wish to thank W. H. McVey for his assistance in planning the experimental program.

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EXPERIMENTAL DATA

TABLE IV

Run	Area	Temp.	Time	H ⁺	NO ₃ ⁻	2 Hg ₂ ⁺⁺	Hg Total
	cm ²	°C	Min.	<u>M</u>	<u>M</u>	<u>M</u>	<u>M</u>
1	79.8	90	0	4.04	4.04	0	0
			5	2.94	3.51	0.21	0.39
			10	2.48	3.52	0.36	0.70
			15	2.11	3.59	0.58	1.03
			20	1.54	3.25	0.85	1.28
			25	1.20	3.21	1.15	1.58
			30	1.01	3.18	1.25	1.71
			35	0.82	3.08	1.62	1.94
			40	0.73	3.10	1.77	2.07
2	79.8	90	0	4.04	4.04	0	0
			5	3.08	3.76	0.24	0.46
			10	0	0	0.43	0.81
			17	1.77	3.57	0.78	1.29
			20	1.53	3.16	0.95	1.29
			26	1.20	3.29	1.27	1.68
			30	1.00	3.25	1.49	1.87
			35	0.81	3.25	1.74	2.09
			40	0.72	3.24	1.90	2.21
3	79.8	90	0	4.12	4.12*	0	0
			10	2.41	3.75	0.44	0.89
			20	1.45	3.55	1.04	1.57
			30	0.93	3.44	1.63	2.07
			40	0.61	3.39	2.00	2.39
4	79.8	90	0	5.51	5.51*	0	--
			5	3.19	4.93	0.33	--
			10	2.13	4.66	0.65	--
			15	1.46	4.49	1.19	--
			20	1.04	4.39	1.70	--
			25	0.72	4.31	2.17	--
			30	0.32	4.21	2.53	--
			35	0.21	4.18	2.79	--
			40	0.08	4.15	3.02	--

* Nitrate Calculated

EXPERIMENTAL DATA

TABLE IV (con't)

Run	Area	Temp.	Time	H ⁺	NO ₃ ⁻	2 Hg ₂ ⁺⁺	Hg Total
	cm ²	°C	Min.	<u>M</u>	<u>M</u>	<u>M</u>	<u>M</u>
5	79.8	90	0	5.51	5.51*	0	0
			5	2.81	4.83	0.47	1.28
			10	1.90	4.61	--	1.93
			15	1.11	4.41	1.98	2.52
			20	0.56	4.27	--	2.94
			25	0.36	4.22	2.85	3.42
			30	0.20	4.18	--	3.59
6	79.8	90	0	1.97	1.97	0	0
			15	1.83	1.97	0.10	0.12
			30	1.62	1.93	0.13	0.22
			45	1.42	1.94	0.34	0.43
			60	1.17	1.85	0.48	0.58
			75	0.99	--	0.62	1.36
			90	0.89	1.87	0.74	0.86
			105	0.79	1.80	--	0.92
			120	0.76	1.85	--	1.00
7	79.8	90	0	2.00	2.00*	0	0
			15	1.79	1.95	0.12	0.13
			30	1.58	1.90	0.24	0.31
			45	1.34	1.84	0.36	0.47
			60	1.16	1.79	0.46	0.58
			75	1.00	1.75	0.58	0.63
			90	0.87	1.72	0.67	0.74
			105	0.83	1.71	0.74	0.80
			120	0.77	1.69	0.81	0.86
8	42.8	90	0	4.09	--	0	--
			6	3.30	--	0.20	--
			10	3.08	--	0.25	--
			15	2.62	--	0.37	--
			20	2.33	--	0.44	--
			25	1.91	--	0.55	--
			30	1.59	--	0.63	--
			35	1.41	--	0.67	--
			40	1.14	--	0.74	--

* Nitrate Calculated

Figure 2

CALCULATED AND EXPERIMENTAL VALUES FOR $4M$ ACID DISAPPEARANCE

Figure 3

CALCULATED AND EXPERIMENTAL VALUES FOR 5.5M ACID DISAPPEARANCE

Figure 4

CALCULATED AND EXPERIMENTAL VALUES FOR 2.0M ACID DISAPPEARANCE

Figure 5

CALCULATED AND EXPERIMENTAL VALUES FOR TOTAL MERCURY WITH 4M ACID

Figure 6

CALCULATED AND EXPERIMENTAL VALUES FOR TOTAL MERCURY WITH 5.5M ACID

Figure 7

CALCULATED AND EXPERIMENTAL VALUES FOR TOTAL MERCURY WITH 2.0M ACID