BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 3466—3470 (1969)

The Indirect Determination of Mercury in an Aqueous Solution using the Ligand Exchange Reaction

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(Received May 15, 1969)

A new method for the indirect determination of mercury in an aqueous solution has been established on the basis of the fact that the absorption and evolution of propylene in the reaction between mercuric ion and propylene take place reversibly and quantitatively under proper conditions. In the method proposed, the propylene in the 1 : 1 π-complex is displaced with such complexing agents as chloride, bromide, iodide and EDTA, and the quantity of the propylene evolved is measured manometrically. By the present method, up to 70 mg Hg can be estimated within $\pm$0.08 mg in about 15 min. Common cations and anions do not interfere. Though silver(I) and palladium ions interfere, their interferences are removed by suitable procedures. By improving the apparatus, it should be possible to estimate much smaller amounts of mercury than the above value.

It has been well established that a mercuric ion in an aqueous solution reacts with olefins to form π-complxes.[1-10] However, the present authors have found that the absorption and evolution of propylene in the reaction between the mercuric ion and propylene take place reversibly and quantitatively under proper conditions. On the basis of this phenomenon, a new method for the indirect determination of mercury in an aqueous solution has been established; in this method the propylene in the π-complex is displaced with complexing agents, such as chloride, bromide, iodide, and EDTA, and the quantity of the propylene evolved is measured manometrically.

Experimental

Apparatus. The quantity of propylene absorbed or evolved was measured at a constant temperature and pressure using the apparatus shown in Fig. 1. The apparatus was made of glass except the parts connecting the sample bottle (B) and the leveler (G) with the cock,6, and the gas-burette, F. Water saturated with propylene was placed in the manometer, E, and the gas-burette, F. An aqueous solution of perchloric acid is placed in (D) and (G), and its acidity is the same as in the sample solution. To the sample solution containing mercury (10—70 mg), 3 m*l* of a 2 M sodium sulfate solution is added; the acidity was adjusted to 0.7M for the use of chloride, bromide, and iodide, or to pH 5 for the use of EDTA, as the complexing agent.

Reagents. *Standard Mercury(II) Solution.* The stock solution of mercury(II) was prepared by dissolving 21.66 g of mercuric oxide (JIS special grade) in 100 m*l* of 1 M perchloric acid. The concentration of mercury was determined by chelometric titration.

Complexing Agent Solutions. Solutions containing sodium sulfate in 2 M, and sodium chloride, sodium bromide or sodium iodide in 0.2 M or EDTA in 0.12 M were prepared. The acidities were 0.7 M in perchloric acid

1) M. A. Bennett, *Chem. Revs.*, **63**, 611 (1962).
2) K. Ichikawa, K. Fujita and O. Itoh, *J. Am. Chem. Soc.*, **84**, 2632 (1962).
3) F. A. Cotton and J. R. Leto, *ibid.*, **80**, 4824 (1958).
4) J. Chatt, *Chem. Revs.*, **48**, 7 (1951).
5) C. W. Whitehead and J. J. Traverso, *J. Am. Chem. Soc.*, **80**, 2182 (1958).
6) M. M. Kreevoy and F. R. Kowitt, *ibid.*, **82**, 739 (1960).
7) K. Ichikawa, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **66**, 1037 (1963).
8) Y. Saito, *Shokubai (Catalyst)*, **9**, 100 (1967).
9) P. M. Henry, *J. Am. Chem. Soc.*, **88**, 1595 (1966).
10) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley & Sons, New York (1965), p. 351.

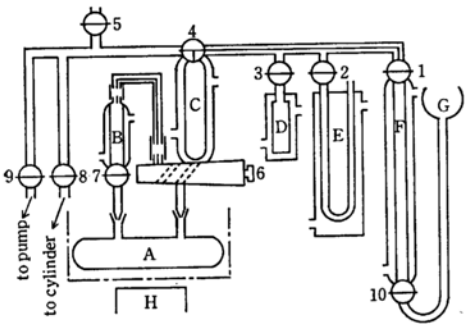

Fig. 1. The apparatus for estimating the quantity of propylene.

A: Reaction vessel
B: Sample bottle
C: Gas holder
D: Vapor pressure adjuster
E: Manometer
F: Gas burette
G: Leveler
H: Magnetic stirrer

except at pH 5 in a solution containing EDTA.

Acetate Buffer. The solution was prepared from sodium acetate and acetic acid.

All the reagents used were of a guaranteed grade.

Procedure. Cocks (1)—(19) are set to the positions shown in Fig. 1, and about 7 m*l* of a sample solution is taken into the sample bottle (B), the capacity of which is about 7 m*l*. Cock (9) is opened, and the inside of the apparatus is evacuated, and the cock closed. To adjust the inside to a constant vopor pressure, Cock (3) is opened and closed. To introduce propylene into the apparatus, Cock (8) is gradually opened after opening Cocks (1) and (10), and Cocks (8) and (10) are closed. Here the meniscus in the gas-burette is brought to the lower part by moving the leveler (G). Then the inside is equilibrated with the atmospheric pressure by regulating Cock (5), and the sample solution is dropped into the reaction vessel (A) (about 30 m*l*) through Cock (7) by operating Cock (6). The solution is stirred by a magnetic stirrer, and propylene is absorbed. After an equilibrium has been established, the stirrer is stopped and Cocks (6) and (7) are set to the positions shown in Fig. 1. The meniscus in the gas-burette is read after the internal pressure has been equilibrated with the atmospheric pressure through a manometer. Seven milliliters of a complexing agent are placed in the (B) and then added to the (A) in the way previously described. The solution is stirred and the meniscus read similarly. The quantity of propylene evolved is calculated by the difference between two readings. All the experiments were carried out at 25°C under an atmospheric pressure.

Results and Discussion

The Absorption of Propylene. Since the reaction between mercuric ions in an aqueous solution and propylene was controlled by the diffusion of propylene into the liquid, the time necessary for 40 mg of mercury ions to reach an equilibrium was measured by the apparatus shown in Fig. 1. The equilibrium was established in about 5 min; the time required was independent of the acidity in the range of pH 0—6. The quantity of propylene absorbed was 4.89 m*l*; this agreed approximately with the theoretical value, showing the composition to be that of a 1 : 1 π-complex. It may be supposed that the formation of the π-complex goes to completion in a short period.

The Evolution of Propylene. To the π-complex obtained in the above experiment there was added a complexing agent containing three times as many moles as mercury, and the quantity of propylene evolved was read against the time. The equilibrium was established within 10 min by adding either a halide solution (0.7 M perchloric acid) or EDTA solution (pH 5) to it. The time required increased in the order of; iodide (2 min)

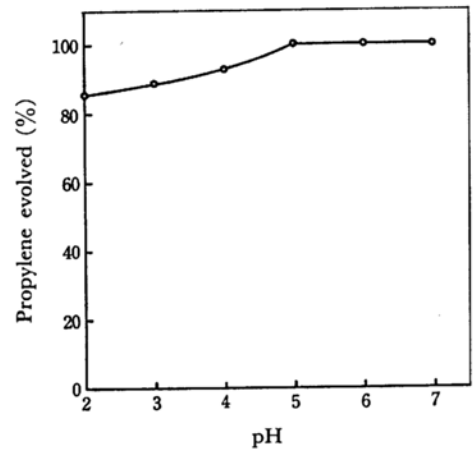

Fig. 2. Evolution of propylene with EDTA. t=25°C, P_{tot}=1 atm, μ=0.8, Mole ratio: [EDTA]/[Hg^{2+}] = 3

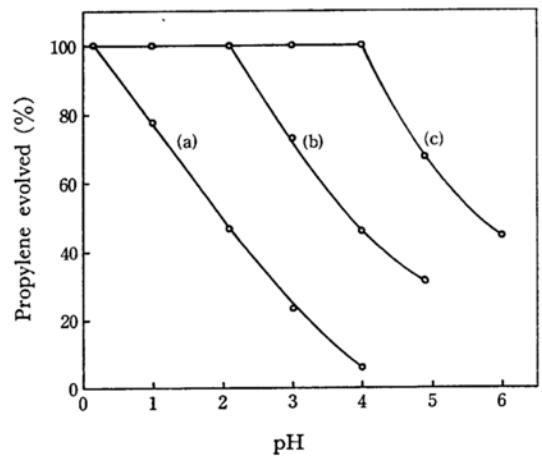

Fig. 3. Evolution of propylene with sodium chloride, sodium bromide and sodium iodide. t=25°C, P_{tot}=1 atm, μ=0.8, Mole ratio: [halide]/[Hg^{2+}]=3, halide: Cl^-, Br^-, I^-
(a) Sodium chloride, (b) Sodium bromide, (c) Sodium iodide

<bromide (6 min)<chloride (8 min) and decreased with an increase in the stability constant of tetrahalogeno-mercuriates.

The Effect of Acidity. The relationship between the pH and the quantity of propylene evolved in a solution containing EDTA and Hg (3 : 1) was shown in Fig. 2. The evolution of propylene was quantitative at pH≧5. The experiment at pH> 7.0 was not feasible since some mercuric compound began to precipitate. The relationship between pH and the quantity of propylene evolved in a solution containing halide and Hg (3 : 1) is also shown in Fig. 3. As can be seen from Fig. 3, propylene is evolved quantitatively in the ranges of the following acidity: molarity of perchloric acid ≧0.7 for chloride, pH≦2.1 for bromide, and pH ≦4.0 for iodide. It can be concluded from these results that the propylene molecule is easily displaced with a halide ion at a lower pH, while it is replaced with EDTA at a higher pH.

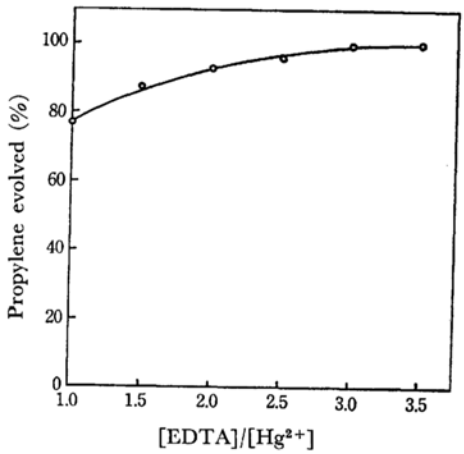

Fig. 4. Evolution of propylene with EDTA. $t=25°C$, $P_{tot}=1$ atm, $\mu=0.8$, pH=5

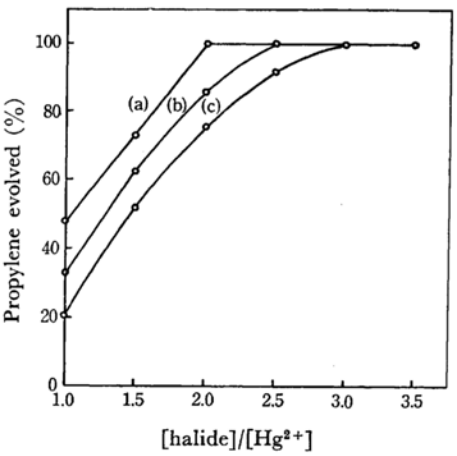

Fig. 5. Evolution of propylene with sodium chloride, sodium bromide and sodium iodide. $t=25°C$, $P_{tot}=1$ atm, $\mu=0.8$, $[HClO_4]=0.7$ N, halide: Cl^-, Br^-, I^-, (a) Sodium iodide, (b) Sodium bromide, (c) Sodium chloride

The effect of the Mole Ratio. The relationship between the mole ratio of [EDTA]/[Hg] or [halide]/[Hg] and the quantity of propylene evolved was shown in Figs. 4 and 5. Propylene was evolved quantitatively under the following conditions: $[EDTA]/[Hg^{2+}]\geqq 3.0$, $[Cl^-]/[Hg^{2+}]\geqq 3.0$, $[Br^-]/[Hg^{2+}]\geqq 2.5$ and $[I^-]/[Hg^{2+}]\geqq 2.0$.

The Calibration Curves. The sample solutions containing 10, 20, 30, 40, 50, 60 and 70 mg of Hg were prepared, and the π-complexes were allowed to form in the apparatus shown in Fig. 1. Then the quantities of propylene evolved on the addition of halides of EDTA were measured. The

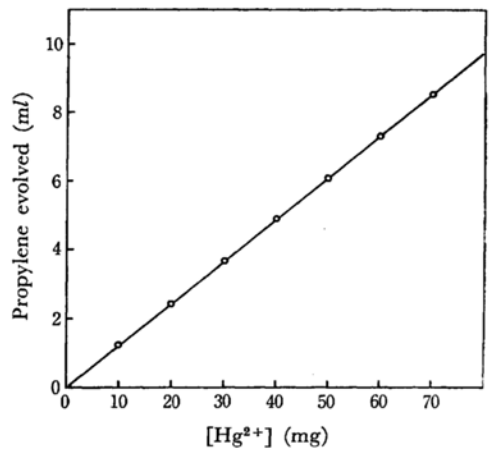

Fig. 6. Calibration curves. $t=25°C$, $P_{tot}=1$ atm

TABLE 1. EFFECTS OF DIVERSE CATIONS AS NITRATES $t=25°C$, $P_{tot}=1$ atm, $[HClO_4]=0.7$ N, Hg^{2+} taken: 40.26 mg

Ion	Mole ratio [ion]/[Hg²⁺]	Propylene evolved ml	Hg²⁺ found mg	Relative error %
Na^+	10.0	4.92	40.34	0.20
K^+	10.0	4.92	40.34	0.20
Mg^{2+}	10.0	4.94	40.50	0.61
Co^{2+}	10.0	4.94	40.50	0.61
Mn^{2+}	10.0	4.92	40.34	0.20
Cu^{2+}	10.0	4.92	40.34	0.20
Zn^{2+}	10.0	4.94	40.50	0.61
Pb^{2+}	10.0	4.92	40.34	0.20
Cd^{2+}	10.0	4.90	40.18	−0.20
Ni^{2+}	10.0	4.94	40.50	0.61
Al^{3+}	10.0	4.92	40.34	0.20
Fe^{3+}	10.0	4.88	40.02	−0.61
Cr^{3+}	10.0	4.94	40.50	0.61
Ag^+	1.0	5.68	46.34	15.68
Pd^{2+}	0.5	2.46	20.66	−49.89
Pd^{2+}	1.0	0.02	1.14	−99.59
Pd^{2+}	3.0	0.00	0.00	−100.00

TABLE 2. EFFECTS OF DIVERSE IONS
$t=25°C$, $P_{tot}=1$ atm, $[HClO_4]=0.7$ N, Hg^{2+} taken: 40.26 mg

Mole ratio Hg^{2+} : Pd^{2+} : Ag^+ : Na^+				Propylene evolved ml	Hg^{2+} found mg	Relative error %
1	1		100	4.92	40.34	0.20
1		1	100	4.56	37.46	−7.12
1	1	1	100	4.52	37.14	−7.94

Mole ratio Hg^{2+} : Cu^{2+} : Mg^{2+} : Zn^{2+} : Mn^{2+} : Al^{3+} : Cr^{3+} : Fe^{3+} : Na^+									Propylene evolved ml	Hg^{2+} found mg	Relative error %
1	10	10	10	10	10	10	10	100	4.94	40.50	0.61

results shown in Fig. 6 were obtained by plotting the quantities of propylene evolved as the ordinate, and the concentration of mercury, as the abscissa. It was confirmed that all the experimental values fall on the same line regardless of the kind of complexing agent. Up to 70 mg Hg gave a straight line.

The Effect of Diverse Ions. The effects of such cations as Na^+, K^+, Mg^{2+}, Cu^{2+}, Co^{2+}, Mn^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+}, Ni^{2+}, Al^{3+}, Fe^{3+} and Cr^{3+} in mole ratios of $[cation]/[Hg^{2+}] \leqq 10$ on the determination of 40.26 mg of Hg were examined, but their interferences were negligible (Table 1). However, Ag^+ and Pd^{2+} interfered seriously. It is generally[10] said that the metals with eight or ten electrons in the *d*-orbital show a tendency to combine with olefins. The fact that no influence was observed on Ni^{2+} (d^8), Zn^{2+} (d^{10}) and Cd^{2+} (d^{10}) shows that the interaction between one of these ions and propylene is negligible. As can be seen from Table 1, the silver(I) ion gave a positive error, while the palladium(II) ion gave a negative error. The former is reasonable since it was confirmed experimentally that the reaction between the silver ion and propylene is quite similar to that between the mercuric ion and propylene, but the silver complex is less stable than the mercuric complex. The latter can also be understood by the following reactions, which were previously proposed by one of the present authors[11]:

$$\text{Propylene} + Pd^{2+} \longrightarrow \text{Acetone} + Pd^* \quad (1)$$

$$Hg^{2+} + \text{Propylene} \longrightarrow Hg^{2+}\cdot\text{Propylene} \quad (2)$$

$$Hg^{2+}\cdot\text{Propylene} + Pd^* \longrightarrow Pd^0 + Hg^0 + \text{Product} \quad (3)$$

Under the present experimental conditions, Reaction (1) goes to completion very fast, while the π-complex produced in Reaction (2) remains stable in the absence of the palladium ion. However, the mercuric complex in the presence of the palladium ion goes to completion in accordance with Reaction (3). These phenomena satisfactorily explain the results shown in Table 1. The interference of the silver ion was eliminated by adding a siutable amount of sodium chloride and by driving off an excess of chloride as hydrogen chloride; that of the palladium ion was also eliminated by adding an alcoholic dimethylglyoxime solution and by precipitating the palladium ion (Table 2). The suspensions were treated much as before.

The effects of such anions as SO_4^{2-}, NO_3^-, ClO_4^-, CH_3COO^-, and $H_2PO_4^-$ in mole ratios of $[anion]/[Hg^{2+}] \leqq 35$ on the determination of 40.12 mg Hg were also examined, but no interference was observed (Table 3). Since the blank value was reduced to zero with an increase in the amount of sodium sulfate, the determination of mercury was always carried out in the presence of a definite amount of sodium sulfate. According to the present procedure, the errors based the temperature change, impurities, *etc.* can be minimized.

In the above experiment, the blank value was

TABLE 3. EFFECTS OF DIVERSE ANIONS AS SODIUM SALTS
$t=25°C$, $P_{tot}=1$ atm, $[HClO_4]=0.7$ N,
Hg^{2+} taken: 40.26 mg

Ion	Mole ratio $[ion]/[Hg^{2+}]$	Blank ml	Hg^{+2} ml	Relative error %
SO_4^{2-}	1	0.68	40.12	
SO_4^{2-}	10	0.52	39.96	−0.39
SO_4^{2-}	35	0.10	40.12	
NO_3^-	1	0.70	40.12	
NO_3^-	10	0.64	40.28	0.39
NO_3^-	35	0.56	40.12	
ClO_4^-	10	0.68	40.12	
ClO_4^-	10	0.58	40.12	
ClO_4^-	35	0.50	39.96	−0.39
CH_3COO^-	1	0.68	40.12	
CH_3COO^-	10	0.64	40.12	
CH_3COO^-	35	0.52	39.96	−0.39
$H_2PO_4^-$	1	0.76	40.28	0.39
$H_2PO_4^-$	10	0.66	40.12	
$H_2PO_4^-$	35	0.38	39.96	−0.39

11) T. Hara, T. Koga and H. Takeda, This Bulletin, **40**, 1634 (1967).

equal to 0.02 ml and was reproducible. The ionic strength in the reaction mixture was approximately 5 throughout the experiment. Up to 70 mg of mercury was determined in the present study, but it should be possible to determine smaller amounts of mercury by improving the apparatus, especially the gas-burette.

The authors wish to thank the Maruzen Sekiyu Co. for its donation of propylene.