

PROMOTING EFFECT OF BENZENE ON REDUCTION OF MERCURY(II) SALTS BY CARBON MONOXIDE IN AQUEOUS MEDIA

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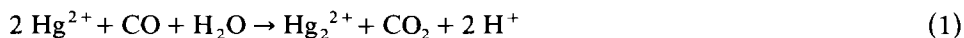
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Summary

The promoting effect of benzene on the reduction of HgX_2 (where $\text{X} = \text{NO}_3^-$, CH_3COO^- , SO_4^{2-}) by carbon monoxide in aqueous media at 298 K, is demonstrated.

It is known [1,2] that Hg^{II} salts can be reduced to Hg^{I} salts by carbon monoxide in perchloric acid solutions by reaction 1:



The rate of the process under these conditions is very low ($6.5 \times 10^{-5} \text{ mol l}^{-1} \text{ min}^{-1}$) and the degree of transformation does not exceed 70% [2]. Harkness and Halpern [1] proposed that reaction 1 proceeds via CO insertion into a Hg-OH_2 bond to form a $[-\text{HgCOOH}]$ fragment, decomposition of which to Hg and CO_2 is very fast.

We have ascertained that the reduction of HgX_2 salts (where $\text{X} = \text{NO}_3^-$, CH_3COO^- , SO_4^{2-}) by carbon monoxide is accelerated considerably by the presence of benzene [3]. This paper presents the results of a study of the kinetics of the reduction of Hg^{II} by carbon monoxide in $\text{Hg}^{\text{II}}\text{-HClO}_4\text{-H}_2\text{O}$ and $\text{Hg}^{\text{II}}\text{-HClO}_4\text{-C}_6\text{H}_6\text{-H}_2\text{O}$ -systems at 298 K.

Experimental

Kinetics of the reaction was studied on a gas flow circulation unit in a shaking reactor with intense agitation. Platinum and calomel electrodes in the reactor made it possible to follow the potential change (φ) of the $\text{Hg}^{\text{II}}\text{-Hg}^{\text{I}}$ redox system in the course of the experiment. Carbon dioxide formed in the experiment, was absorbed in a special absorber containing a solution of KOH. At the end of each experiment, the content of monovalent mercury was determined analytically.

Results and discussion

The experimental data obtained show that Hg^{II} acetate is reduced in perchloric acid at a rate of $5 \times 10^{-4} \text{ mol l}^{-1} \text{ min}^{-1}$. The reaction can be observed by a shift of the potential (φ) by 0.2 V to the cathode region. Variation of salt concentration, acidity of the solution and temperature of the experiment affects the rate of reaction insignificantly. Compared to that of $\text{Hg}(\text{CH}_3\text{COO})_2$, CO absorption by HgCl_2 , $\text{Hg}(\text{NO}_3)_2$ and HgSO_4 is slower still.

Addition of benzene to the reaction system causes a great increase in the reaction rate. The obtained kinetic and potentiometric data of Hg^{II} acetate reduction are shown in Fig. 1. Irrespective of the nature of the anion (NO_3^- , CH_3COO^- , SO_4^{2-}), the kinetic curves are of autocatalytic character. The autocatalysis can probably be associated with the formation of active, mixed carbonyl complexes of lower-valent mercury during the course of the reaction, as shown for similar reactions with Pd^{II} [4]. The maximum rate of Hg^{II} to Hg^{I} reduction is observed with a benzene content in the reaction medium of 1.4×10^{-1} to $2.8 \times 10^{-1} \text{ mol l}^{-1}$ (Fig. 2, curves 1,2 and 3). We have also found a similar relationship of $W = f(C(\text{C}_6\text{H}_6))$ for reduction of Li_2PdCl_4 by carbon monoxide (Fig. 2, curve 4).

By varying the acidity of the medium, the process is made to proceed most effectively in $4.0 \text{ mol l}^{-1} \text{ HClO}_4$ (Fig. 3). Inhibition of the reaction in diluted solutions is, evidently, caused by hydrolysis of the Hg^{II} salts. A cause of the decrease of activity in concentrated media is less clear. It may be due to a decrease of water

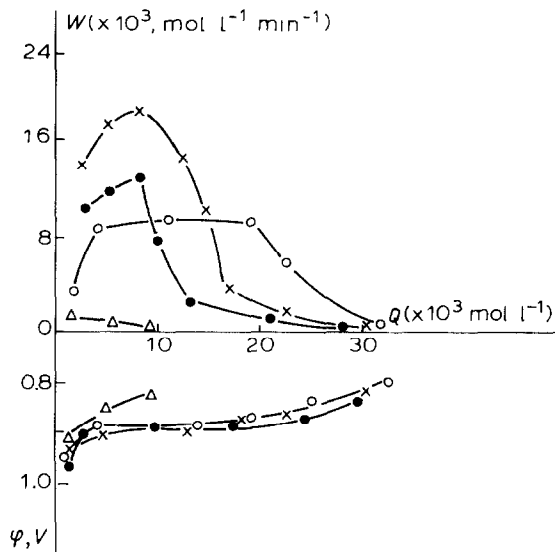


Fig. 1. Reduction of $\text{Hg}(\text{CH}_3\text{COO})_2$ by carbon monoxide in the presence of benzene at 298 K. C (mol l^{-1}): $C(\text{HClO}_4) = 4.0$; $C(\text{Hg}^{\text{II}}) = 4.4 \times 10^{-2}$; $\text{CO} = 100\%$

- Δ - 0.0 $\text{mol l}^{-1} \text{ C}_6\text{H}_6$
- \bullet - $1.4 \times 10^{-1} \text{ mol l}^{-1} \text{ C}_6\text{H}_6$
- \times - $2.8 \times 10^{-1} \text{ mol l}^{-1} \text{ C}_6\text{H}_6$
- \circ - $4.2 \times 10^{-1} \text{ mol l}^{-1} \text{ C}_6\text{H}_6$

Q = volume of gas absorbed in the reaction; vol. solution = 40 cm^3 .

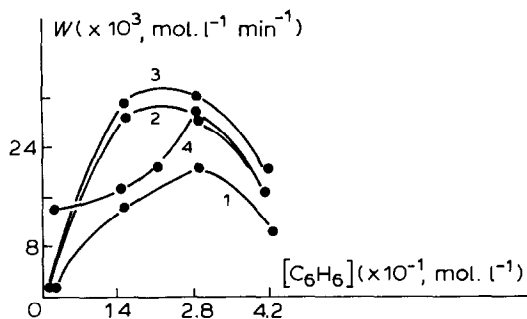


Fig. 2. Effect of benzene concentration on the rate of reduction of Hg^{II} and $PdCl_4^{2-}$ salts by carbon monoxide. 298 K, C (mol l^{-1}): $C(Hg^{II}) = 4.4 \times 10^{-2}$; $C(HClO_4) = 4.0$; $C(Pd^{II}) = 1.1 \times 10^{-2}$; $CO = 100\%$
 1 – $Hg(CH_3COO)_2$
 2 – $HgSO_4$
 3 – $Hg(NO_3)_2$
 4 – Li_2PdCl_4 .

and benzene activity or a change of the equilibrium of the benzene mercuriation reaction (eq. 2) [5]:



We have assumed the promoting effect of benzene to result from the formation of $[Hg^{II} \cdot C_6H_6]$ electron donor-acceptor complexes and from the subsequent fast displacement of benzene by carbon monoxide. In fact, during the first minute of contact of CO with a benzene-containing Hg^{II} salt solution the gas phase volume increases, and then follows the process of CO absorption by the Hg^{II} solution. Comparison of the total gas consumed (Q_{total}), the gas isolated from the solution ($Q_{isolat.}$) and the difference between their volumes (see Table 1) shows that stoichiometric absorption of carbon monoxide, corresponding to 100% transformation of Hg^{II} to Hg^I , takes place for all salts except $HgCl_2$.

The exception is $HgCl_2$; reduction of this compound does not occur, as is

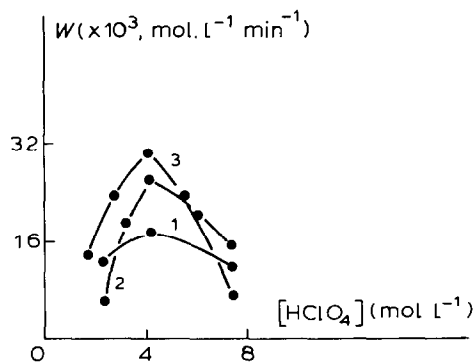


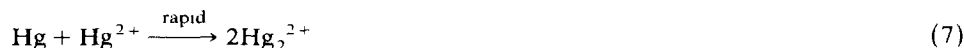
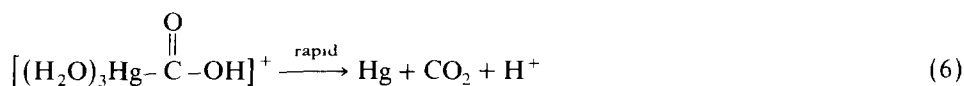
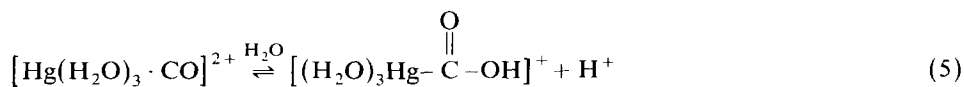
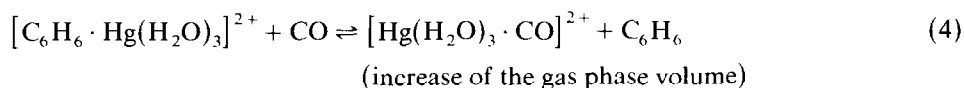
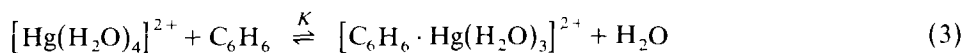
Fig. 3. Effect of acidity of the solution upon the rate of reduction of Hg^{II} salts by carbon monoxide in the presence of benzene at 298 K. C (mol l^{-1}): $C(Hg^{II}) = 4.4 \times 10^{-2}$; $C(C_6H_6) = 2.8 \times 10^{-1}$; $CO = 100\%$
 1 – $Hg(CH_3COO)_2$
 2 – $HgSO_4$
 3 – $Hg(NO_3)_2$.

TABLE I
CORRELATION BETWEEN ISOLATED AND ABSORBED GAS VOLUMES

HgX ₂ (4.4 × 10 ⁻² mol l ⁻¹)	C ₆ H ₆ (× 10 ⁻¹ mol l ⁻¹)	Q _{total} [*] (cm ³)	Q _{isolat} [*] (cm ³)	Q _{total} - Q _{isolat} [*] (cm ³)
Hg(CH ₃ COO) ₂	1.4	28.3	8.3	20.0
	2.8	33.3	10.5	22.8
	4.2	34.3	13.0	21.3
HgSO ₄	1.4	30.1	10.5	19.0
	2.8	35.0	15.0	20.0
	4.2	32.4	12.8	19.6
Hg(NO ₃) ₂	1.4	32.0	13.3	19.0
	2.8	36.4	17.3	19.0
	4.2	33.8	17.0	18.0
HgCl ₂	1.4	15.7	12.8	2.9
	2.8	18.3	14.2	4.1
	4.2	19.3	14.0	5.3

confirmed by qualitative reactions. The insignificant absorption of carbon monoxide probably leads to carbonyl complex formation. The lack of activity of HgCl₂ is due to the fact that Cl⁻ is strongly bound with the central ion; as a result, the complex hardly dissociates in water [6]. For the same reason, Hg^{II} acetate is reduced at a lower rate compared to the sulphate or nitrate of Hg^{II}; in aqueous solutions, Hg^{II} acetate is present in the form of [HgCH₃COO]⁺, Hg(CH₃COO)₂ and [Hg(CH₃OO)₃]⁻ complexes which also dissociate poorly [7]. On the contrary, HgSO₄ and Hg(NO₃)₂ possess ionic character, dissociate well in water and are present in the form of diaquo complexes of linear structure [Hg(H₂O)₂]²⁺ [5]. Diaquo complexes can transform into coordinatively saturated tetraaquo or even hexaquo complexes.

On the basis of literature [1,2,8] and our experimental data we propose the mechanism of Hg^{II} salt reduction by carbon monoxide as follows:



The formation of electron donor-acceptor complexes of benzene with Hg^{II} is confirmed by UV data currently available in the literature, i.e. aromatic hydro-

carbons yield new bands with λ_{\max} at 270–300 nm [9,10]. This fact is attributed to the formation of charge transfer complexes in the solution. Calculation gives $K = 90$.

Thus, the promoting effect of benzene consists of the formation of prereaction complexes with Hg^{II} compounds which makes much easier further insertion of carbon monoxide into the coordination sphere of the complex, forming carbonyl and hydrocarbonyl complexes (reactions 4 and 5). The ready displacement of C_6H_6 by CO (see Table 1) is due to the stronger Hg–CO bond. A modifying effect is, however, exhibited until a certain degree of screening (solvation) of the Hg^{II} complex by benzene molecules: above $2.0 \times 10^{-1} \text{ mol l}^{-1}$ benzene, the reaction starts to be inhibited.

We consider that the effect described here is an example of a general phenomenon of promotion of reaction by insertion into the inner sphere of complexes (weak interaction effect) of weakly bound labile ligands. Other typical examples are the modifying effect of dioxygen [11] on the reduction of Pd^{II} by carbon monoxide and the similar effect of dioxane on this reaction [12].

Realization of this effect would require the following:

1) Kinetic lability of the ligand forming the prereaction complex, i.e. $[-\text{M} \cdot \text{C}_6\text{H}_6]$; $[-\text{M} \cdot \text{O}_2]$; $[-\text{M} \cdot \text{dioxane}]$.

2) Rather low thermodynamic stability of the prereaction complex resulting in easy displacement of the ligand by a more tightly bound ligand (i.e. CO).

Hence, ligands of C_6H_6 , O_2 and dioxane type occupy a considerable volume in the inner sphere, which rapidly becomes free due to displacement by another ligand (CO). The latter participates in a further stoichiometric or catalytic chemical reaction.

References

- 1 A.C. Harkness and J. Halpern, J. Amer. Chem. Soc., 83,5 (1961) 1258.
- 2 V.D. Markov and A.B. Fasman, Zh. Fiz. Khimii., 7 (1966) 1564.
- 3 E.L. Kuksenko, V.A. Golodov and D.V. Sokolsky, Pat. USSR 937443, Bjull. 23, publ. 26.06.82.
- 4 V.A. Golodov, Yu.L. Sheludjakov, R.I. De and V.K. Fokanov, Kinetica i Kataliz, 18 (1977) 2343.
- 5 K.K. Ingold, Structure and Mechanism in Organic Chemistry. Cornell University Press, Ithaca, New York, 1953.
- 6 L.N. Baljatinskja, Uspekhi Khimii, 4 (1979) 772.
- 7 A.P. Kreshkov and L.N. Baljatinskaja, Zh. Obshchej Khimii, 412 (1971) 276.
- 8 J. Halpern, Comments Inorg. Chem., 1 (1981) 3.
- 9 R.G. Pearson, J. Amer. Chem. Soc., 85 (1963) 3533.
- 10 E.N. Gurjanova, I.P. Goldshtein and I.P. Romm Donor-acceptor bond, Khimija, Moscow, 1973.
- 11 V.A. Golodov, E.L. Kuksenko and D.V. Sokolsky, Dokl. Akad. Nauk SSSR, 272 (1983) 628.
- 12 V.A. Golodov, A.B. Fasman, G.G. Kutjukov and V.V. Roganov, Zh. Fiz. Khimii, 41 (1967) 1085.