Kinetics of electrochemical reduction of 2-carbomethoxy-1,1-dichloro-2-methylcyclopropane by the double mediator system anthracene—Pt^{II}, Pd^{II}, and Ni^{II} complexes of cyclic aminomethylphosphines

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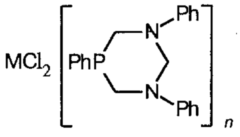
Effective rate constants of homogeneous reduction of 2-carbomethoxy-1,1-dichloro-2-methylcyclopropane have been calculated by the polarographic method of determining the catalytic increase in the limiting current of the reduction wave of mediators, *i.e.*, individual complexes of platinum, palladium or nickel with cyclic aminomethylphosphines and their combination with anthracene radical anions. Platinum compounds show higher catalytic activity than palladium and nickel complexes in direct reduction with metallocomplexes. The catalytic activity of a double mediator system for the majority of metallocomplexes is higher than the total catalytic activity of the individual metallocomplex and organic carrier.

Key words: metal complexes; aminomethylphosphines; catalysis; organic electron carrier; *gem*-dichlorocyclopropane.

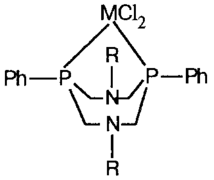
Previously[1,2] we found catalysis by Pt^{II}, Pd^{II}, Rh^{II}, Ni^{II}, and Co^{II} ions of the homogeneous reduction of *gem*-dichlorocyclopropanes by radical anions of organic compounds. Metal ions do not noticeably affect the reduction in the absence of an organic carrier. The synergistic effect observed in the double mediator system including an organic electron carrier and metal ion is of doubtless theoretical interest and can be helpful for the development of new highly efficient catalytic systems. This communication continues the study of processes involving double mediator systems and is devoted to the study of the kinetics of the homogeneous reduction of 2-carbomethoxy-1,1-dichloro-2-methylcyclopropane with the double mediator system consisting of an organic electron carrier and Pt^{II}, Pd^{II}, or Ni^{II} complexes of some cyclic aminomethylphosphines.

Experimental

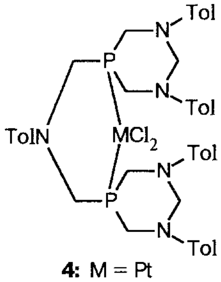
Kinetics of homogeneous reduction was studied by polarography in DMF with 0.1 *M* Bu_4NBF_4 as a base. Known procedures[2] were used for the purification of the solvent and the base salt and for polarographic measurements and calculation of kinetic parameters. Characteristics of the capillary: $m_{Hg} = 0.71$ mg s^{-1}, $t_1 = 0.5$ s; the frequency of the potential changing was 10 Hz, base mercury with a potential of −0.14 V rel. SCE served as the reference electrode. The procedures for the synthesis, purification, and identification of complexes (**1**—**7**) have been described previously.[3,4]



1: M = Ni, *n* = 2
2: M = Pt, *n* = 3



3: M = Pt, R = Bz
5: M = Pd, R = Tol
6: R = Bz



4: M = Pt
7: M = Pd

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Results and Discussion

One irreversible (according to the method of commutator polarography) reduction wave is observed on the polarograms of metallocomplexes **1**—**7** studied (Table 1). The reduction potentials $E_{1/2}$ of the complexes depends not only on the nature of the central ions but also on that of the ligands. The complexes of Pt^{II} are more difficult to reduce than the corresponding complexes of Pd^{II} and Ni^{II}. The influence of ligands on the ease of complex reduction is similarly manifested in the case of Pt^{II} and Pd^{II} complexes. For Pt^{II} complexes going from compound **3** to compound **4**, the $E_{1/2}$ value shifts to more negative values. The analogous dependence is observed in the case of Pd^{II} complexes (compounds **6** and **7**) as well.

The reduction of metal complexes by phosphine ligands is accompanied, as a rule, by the transfer of an electron to the central ion.[5] It is likely that the reduction of the complexes studied also results in a change in the oxidation state of the central ion.

The introduction of a substrate into the solution of complexes **1** and **5** results in a polarogram corresponding to the additive curve of the individual metallocomplex and the substrate. In the case of other complexes, the limiting current of the reduction wave of the metallocomplex increases, which indicates the catalytic reduction of the substrate. In this process, the complexes of metals with a low oxidation degree (0 or 1) are the catalytically active forms. The effective rate constants ($k^{MC}{}_{eff}$) of substrate reduction presented in Table 2 were calculated from the increases in the limiting current. The catalytic activity of the complexes as well as the redox properties depend on the nature of the central ion and the ligand surroundings. Pt^{II} complexes are more efficient (2—4 times) than those of Pd^{II} with the same ligand surroundings.

The influence of the nature of the ligand can be seen using Pd^{II} complexes as examples. Pd^{II} complexes can be placed, according to their efficiency, in the series **6** > **7** > **5**. The metallocomplexes demonstrate different activity in the reduction of *gem*-dihalocyclopropane by the double mediator system anthracene radical anions—metallocomplex. The activity of **3** somewhat decreases under these conditions. This complex is the most active for direct reduction with metallocomplexes (see Table 2). The experimentally measured effective rate constant ($k^{An,MC}{}_{eff}$) is lower than the calculated total of the rate constants of the reduction by metallocomplexes and by anthracene radical anions separately. In contrast, less active complexes in a simple mediator system turn out to be more active. Pt^{II} (**4**) and Pd^{II} (**7**) complexes, which occupy an intermediate position in the series of simple mediator systems, are the most active in double mediator reduction. Their activity is almost the same as that of the corresponding metal ions,[6] and the effective rate constant of the reduction of the substrate by two mediators (metallocomplex—organic carrier) is 3.6—3.7 times the calculated additive rate constant of the individual metallocomplex and the organic carrier. It is likely that synergism appears in this case. A less pronounced but noticeable synergistic effect is observed in the cases of **1**, **2**, and **5** as well.

As a rule, the exponential dependence of the effective rate constant on $E_{1/2}$ of the carrier is observed for the homogeneous reduction of various substrates by means of organic electron carriers.[7,8] There is not such a distinct dependence for double mediator reduction in the series of Pt^{II} and Pd^{II} complexes, but the tendency is observed. The complexes reduced at more negative potentials manifest higher catalytic activity. The absence

Table 1. Electrochemical characteristics of reduction waves for metallocomplexes **1**—**7***

Metallocomplex	$-E_{1/2}$/V	$i_{пр}\cdot 10^4$ /A cm^{-2}	$\Delta E/\Delta \lg \frac{i}{i_{lim}-i}$ /mV
1	0.63	3.3	200
2	0.98	5.1	150
3	1.70	3.9	70
4	1.82	5.2	110
5	0.78	3.3	350
6	0.80	2.7	380
7	1.3	3.8	200

DMF, 0.1 *M* Bu_4NBF_4 (base), 25 °C, $C = 10^{-3}$ *M*.

Table 2. Kinetics of reduction of 2-carbomethoxy-1,1-dichloro-2-methylcyclopropane by individual metallocomplexes and in combination with anthracene radical anions*

Metallocomplex	$k^{MC}{}_{eff}\cdot 10^{-2}$ /M^{-1} s^{-1} [a]	$k^{An,MC}{}_{eff}\cdot 10^{-3}$ /M^{-1} s^{-1} [b]
1	—	1.1
2	0.6	2.1
3	7.6	0.6
4	2.7	3.4
5	—	1.0
6	2.1	0.9
7	1.2	3.0

* DMF, 0.1 *M* Bu_4NBF_4 (base), 25 °C, $C^{An} = C^{MC} = 1\cdot 10^{-3}$ *M*, $C^{BX} = 1\cdot 10^{-2}$ *M*.

[a] $k^{MC}{}_{eff}$ is the effective rate constant of reduction by the metallocomplexes generated in the electrochemical reduction of complexes **1**—**7**.

[b] $k^{An,MC}{}_{eff}$ is the effective rate constant of reduction by the metallocomplex in combination with the anthracene radical anion; calculated from the catalytic increase in the limiting current of the first wave of anthracene reduction in the presence of the metallocomplex and substrate; the rate constant of the homogeneous reduction of the substrate by anthracene radical anions without metallocomplexes is $6.7\cdot 10^2$ M^{-1} s^{-1}.

of the pronounced correlation attests to a complicated mechanism of the process with the double mediator system. For the homogeneous reduction of *gem*-dichlorocyclopropane by the double mediator system organic electron carrier—metal ion, we also proposed, in addition to the direct reduction of the substrate by the organic carrier, the homogeneous reduction of the metals to lower oxidation degrees by the organic ion carrier and the participation of these metal ions in the reduction.[2] Probably, the same mechanism takes place in the system organic carrier—metallocomplex. It seems that one cannot exclude the possibility of the formation of more active metallocomplexes with the participation of the organic carrier as a ligand. Phenomena related to the heterogeneity of the generation of the active form of the metallocomplex may be one of the reasons for the different activity of metallocomplexes in the simple mediator reduction of *gem*-dichlorocyclopropane. The catalytic activity estimated by the usual electrochemical methods, apparently, does not completely correspond to the homogeneous catalytic properties of metallocomplexes. Perhaps, the homogeneous catalytic properties of metallocomplexes can be estimated more exactly using the double mediator system, because in this case the active form of the metallocomplex is generated under homogeneous conditions.

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Thus, the complexes of Pt^{II} with cyclic aminomethylphosphines manifest higher catalytic activity than the corresponding Pd^{II} and Ni^{II} complexes for the electrochemical reduction of 2-carbomethoxy-1,1-dichloro-2-methylcyclopropane in DMF by a simple mediator system.

For the majority of Pt^{II}, Pd^{II}, and Ni^{II} complexes, the catalytic activity of the double mediator system metallocomplex—anthracene radical anion for analogous processes is higher than the total of the catalytic activity of the individual metallocomplex and the organic electron carrier.

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