# The kinetics of the homogeneous reduction of organobromo and organochloro compounds by anthracene radical anions in the presence of $Ni^{II}$ and $Co^{II}$ ions

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The effect of $Ni^{II}$ and $Co^{II}$ on the kinetics of the homogeneous reduction of some aromatic, aliphatic, and cyclic organobromo and organochloro compounds by anthracene radical anions has been studied by the polarographic method. It has been shown that the catalytic action of the metal ions increases as the reducibility of the organohalide compounds decreases.

**Key words:** homogeneous reduction, organohalide compound, radical anion, metal ions, catalysis.

Previously[1—3] we reported the acceleration of the homogeneous reduction of geminal dichlorocyclopropanes by radical anions of organic compounds in the presence of ions of some transition metals. As an extention of this work, we have studied the kinetics of the homogeneous reduction of some aromatic, aliphatic, and cyclic organobromo and organochloro compounds by anthracene radical anions in the presence of $Ni^{II}$ and $Co^{II}$ ions.

## Experimental

The kinetics of homogeneous reduction were studied by polarography. The procedures of the polarographic measurements and calculations of kinetic parameters have been described previously.[1] We used a capillary with the following characteristics: $m_{Hg} = 1.229 \cdot 10^{-4}$ g s$^{-1}$, $t = 0.5$ s; bottom mercury with a potential of −0.5 V rel. SCE was used as the reference electrode; the temperature was 25 °C. Anthracene (purity grade "spectrally pure"), $Ni(BF_4)_2 \cdot 6H_2O$, and $Co(BF_4)_2 \cdot 6H_2O$ (purity grade "pure") were used without further purification.

Organohalide compounds were purified according to standard procedures, DMF was purified by the known procedure,[4] dimethyl sulfoxide (DMSO) was stored over KOH for three days and then purified similarly. Acetonitrile was purified by triple fractional distillation over phosphorous pentoxide according to the known procedure,[5] and pyridine was purified as recommended in Ref. 6.

Supporting salts based on tetrafluoroborates were prepared from aqueous solutions of the corresponding acids and bases. All supporting salts were twice recrystallized from a water—ethanol mixture and dried at 50—60 °C *in vacuo*.

## Results and Discussion

Organohalide compounds (RX) reducible at more negative potentials than the first wave of anthracene reduction were used for the investigation (Table 1). All of them are irreversibly reduced using two electrons per molecule. The effective rate constants of the homogeneous reduction of RX by anthracene radical anions in the presence of $Ni^{II}$ ($k^{Ni}{}_{eff}$) and $Co^{II}$ ($k^{Co}{}_{eff}$) ions and in their absence ($k^{A}{}_{eff}$) were calculated from the value of the catalytic increase in the limiting current associated with the first wave of anthracene reduction. The values of $k_{eff}$ thus obtained are listed in Table 1. The data found previously for geminal dichlorocyclopropanes are also placed there for comparison. Evidently, in the absence of metal ions there occurs a process typical of homogeneous reduction of organic compounds by radical anions.[3] Namely, the effective rate constant decreases with the increase in the potential difference of the reduction half-waves for the carrier (A) and substrate (RX). For compounds **9** and **10**, which are very difficult to reduce, the reaction rate becomes so insignificant that it cannot be measured by polarography. The $k_{eff}$ values of these compounds were determined by extrapolating the dependence $\log k^{A}{}_{eff}$ *vs.* $(E^{A}{}_{1/2} - E^{RX}{}_{1/2})$.

The presence of $Ni^{II}$ ions accelerates the homogeneous reduction by anthracene radical anions for all of the substrates ($k^{Ni}{}_{eff} > k^{Co}{}_{eff}$). As a rule, the catalytic effect of $Ni^{II}$ ions increases with their concentration. In the series of compounds studied an interesting relationship was found: the more cathodic $E^{RX}{}_{1/2}$, the higher the

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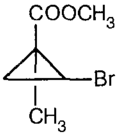
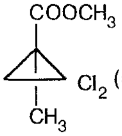
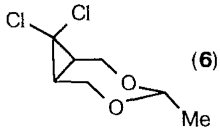
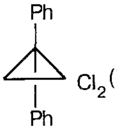
**Table 1.** Effective rate constants of the homogeneous reduction of organohalide compounds **1—10** by anthracene radical anions in the presence of Ni$^{II}$ and Co$^{II}$ ions and in their absence

| Substrate | $-E^{RX}_{1/2}$/V rel. Hg/I$^-$ | $k^A_{eff}$/mol$^{-1}$L s$^{-1}$ | $\upsilon$* | $k^{Ni}_{eff}$/mol$^{-1}$ L s$^{-1}$ | $k^{Co}_{эф}$/mol$^{-1}$ L s$^{-1}$ |
|---|---|---|---|---|---|
| $C_6H_5CH_2Cl$ (**1**) | 1.81 | $9.6 \cdot 10^4$ | 1.0 | $1.1 \cdot 10^5$ | $8.0 \cdot 10^4$ |
| $C_4H_9Br$ (**2**) | 1.93 | $5.6 \cdot 10^2$ | 1.0<br>2.0 | $8.6 \cdot 10^2$<br>$3.0 \cdot 10^3$ | $9.0 \cdot 10^1$<br>$1.7 \cdot 10^3$ |
|  (**3**) | 1.98 | $2.4 \cdot 10^2$ | 1.0<br>2.0<br>2.0 | $1.3 \cdot 10^3$<br>$1.6 \cdot 10^3$<br>$2.2 \cdot 10^3$ | $1.7 \cdot 10^3$<br>$4.3 \cdot 10^3$<br>$5.1 \cdot 10^3$ |
| $C_3H_7Br$ (**4**) | 1.98 | $8.4 \cdot 10^2$ | 1.0<br>2.0<br>2.0** | $1.2 \cdot 10^3$<br>$1.2 \cdot 10^3$<br>$4.0 \cdot 10^3$ | $8.0 \cdot 10^2$<br>$2.5 \cdot 10^3$<br>$2.3 \cdot 10^3$ |
|  (**5**) | 2.07 | $6.7 \cdot 10^2$ | 1.0<br>2.2 | $3.6 \cdot 10^3$<br>$1.3 \cdot 10^4$ | $1.4 \cdot 10^3$ |
|  (**6**) | 2.12 | $2.2 \cdot 10^2$ | 1.0 | $1.3 \cdot 10^3$ | $9.0 \cdot 10^2$ |
|  (**7**) | 2.13 | $1.0 \cdot 10^2$ | 1.0 | $5.5 \cdot 10^3$ | $2.6 \cdot 10^2$ |
| $C_6H_5Br$ (**8**) | 2.13 | $3.0 \cdot 10^1$ | 1.0<br>2.0 | $2.1 \cdot 10^3$<br>$4.1 \cdot 10^3$ | $4.5 \cdot 10^2$<br>$1.0 \cdot 10^3$ |
| $C_6H_5Cl$ (**9**) | 2.26 | 3.0 | 1.0<br>2.0 | $2.5 \cdot 10^2$<br>$2.6 \cdot 10^2$ | $2.0 \cdot 10^2$<br>$3.0 \cdot 10^1$ |
| $C_4H_9Cl$ (**10**) | 2.38 | 0.2 | 1.0<br>2.0<br>2.0** | $3.0 \cdot 10^2$<br>$5.0 \cdot 10^2$<br>$6.0 \cdot 10^2$ | $4.0 \cdot 10^1$<br>$3.0 \cdot 10^2$<br>$4.0 \cdot 10^2$ |

*Note.* Reduction conditions: DMF, 0.1 mol L$^{-1}$ Bu$_4$NI as a supporting salt, 25 °C, $C^A = 1 \cdot 10^{-3}$ mol L$^{-1}$, $C^{RX} = 1 \cdot 10^{-2}$ mol L$^{-1}$.

* $\upsilon = C^M/C^A$. ** $C^{RX} = 2 \cdot 10^{-2}$ mol L$^{-1}$.

ratio $k^{Ni}_{eff}/k^A_{eff}$ (Fig. 1, *a*). Evidently, the less reducible the substrate, the stronger the catalytic effect of Ni$^{II}$ ions.

The action of Co$^{II}$ ions is not so unambiguous. In the reduction of compounds **1—2** they manifest both inhibiting and catalytic effects depending on the concentrations of Co$^{II}$ ions and the substrate (see Table 1). Co$^{II}$ ions catalyze the homogeneous reduction of other substrates by anthracene radical anions. The catalytic effect of the Co$^{II}$ ions is stronger for the less reducible substrates, as in the case of Ni$^{II}$ ions (Fig. 1, *b*).

The results obtained attest that Ni$^{II}$ and Co$^{II}$ catalyze the homogeneous reduction of aromatic, aliphatic, and cyclic organobromo and organochloro compounds by anthracene radical anions in DMF in the presence of 0.1 mol L$^{-1}$ Bu$_4$NI (see Table 1), other electrolytes (Table 2), and in a 0.1 mol L$^{-1}$ solution of Bu$_4$NI in other aprotic solutions (Table 3). Previously[1—3] we reported about the catalytic action of other metal ions

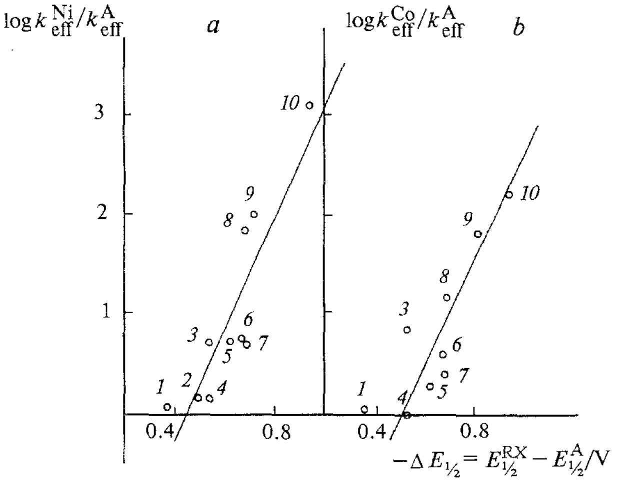


**Fig. 1.** The relationship between the values of log($k^M_{eff}/k^A_{eff}$) for the homogeneous reduction of organohalide compounds **1—10** and the potential differences of the reduction half-waves of anthracene and the substrate. M = Ni$^{II}$(*a*), Co$^{II}$(*b*).

($Pt^{II}$, $Pd^{II}$, and $Rh^{III}$) and possibility of using other radical anions.

**Table 2.** Effective rate constants of the homogeneous reduction of 2-carbomethoxy-2-methyl-1,1-dichlorocyclopropane in the presence of $Ni^{II}$ and $Co^{II}$ ions and in their absence

| Supporting salt | $k^{A}_{eff} \cdot 10^{-2}$ /mol$^{-1}$ L s$^{-1}$ | $k^{Co}_{eff} \cdot 10^{-3}$ /mol$^{-1}$ L s$^{-1}$ | $k^{Ni}_{eff} \cdot 10^{-3}$ /mol$^{-1}$ L s$^{-1}$ |
|---|---|---|---|
| $(C_3H_7)_4NI$ | 6.0 | 1.6 | 2.0 |
| $(C_4H_9)_4NI$ | 6.3 | 1.2 | 1.8 |
| $(C_4H_9)_4NBr$ | 5.7 | 1.3 | 2.1 |
| $(C_2H_5)_4NBF_4$ | 1.1 | 1.7 | 4.4 |
| $(C_2H_5)_4NClO_4$ | 5.6 | 1.3 | 3.0 |
| $(C_4H_9)_4NBF_4$ | 9.0 | 1.5 | 1.4 |

*Note.* Reduction conditions:
DMF, $C^{M} = C^{A} = 1 \cdot 10^{-3}$ mol L$^{-1}$.

**Table 3.** Effective rate constants of the homogeneous reduction of 2-carbomethoxy-2-methyl-1,1-dichlorocyclopropane in the presence of $Ni^{II}$ and $Co^{II}$ ions and in their absence

| Solvent | $k^{A}_{eff} \cdot 10^{-2}$ /mol$^{-1}$ L s$^{-1}$ | $k^{Co}_{eff} \cdot 10^{-3}$ /mol$^{-1}$ L s$^{-1}$ | $k^{Ni}_{eff} \cdot 10^{-3}$ /mol$^{-1}$ L s$^{-1}$ |
|---|---|---|---|
| DMSO | 5.4 | 2.0 | 1.3 |
| Pyridine | 6.0 | 2.7 | 1.8 |
| DMSO | 6.3 | 1.2 | 1.8 |
| Acetonitrile | 9.2 | 2.7 | 4.4 |

*Note.* Reduction conditions: 0.1 mol L$^{-1}$ $Bu_4NI$, $C^{M} = C^{A} = 1 \cdot 10^{-3}$ mol L$^{-1}$.

Thus, from our experimental data it follows that the binary mediator system "organic carrier—transition metal ion" is suitable for the electrocatalytic reduction of a wide range of organobromo and organochloro compounds in aprotic media with tetralalkylammonium salts as supporting electrolytes. In all of the cases, synergism is manifested: the binary mediator system displays more pronounced catalytic properties than the radical anions or metal ions taken alone.

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