

1,2-Dihydro-1,2,4,3-triazaphospholo[4,5-*a*]quinolines as electron carriers in the electrochemical reduction of 1,1-dichloro-2-methoxycarbonyl-2-methylcyclopropane

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Electrochemical reduction of 1-X-1-R¹-5-methyl-2-phenyl-7-R²-1,2-dihydro-1,2,4,3-triazaphospholo[4,5-*a*]quinolines **1–5** (1: X is the lone electron pair (LEP), R¹ = Et₂N, R² = Me; 2: X = LEP, R¹ = Ph, R² = H; 3: X = S, R¹ = Et₂N, R² = H; 4: X = LEP, R¹ = Et₂N, R² = H; 5: X = LEP, R¹ = MeO, R² = H) in DMF with 0.1 M Bu₄Nl as supporting electrolyte is reversible and results in metastable radical anions. Radical anions of compounds **1–3** efficiently reduce 1,1-dichloro-2-methoxycarbonyl-2-methylcyclopropane both in the presence and in absence of Ni^{II} ions. Effective reduction rate constants have been evaluated.

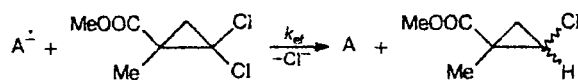
Key words: electrochemistry, mediator, reduction, kinetics, 8*π*,*π*-heterocycles, 1,2,4,3-triazaphospholo[4,5-*a*]quinolines, *gem*-dichlorocyclopropane.

Recently, mediatory electrochemical processes are considered to be promising in the electrochemical synthesis of organic compounds. Organic compounds, metal ions, and complexes are used as electron carriers. Double mediator systems, consisting of an organic electron carrier and a metal ion (complex), are also studied.^{1–6} The problem arises of producing new mediators with preset redox properties for fine control over the rates and selectivity of processes. In this work, new representatives of 8*π*,*π*-electron heterocyclic systems,^{7,8} 1,2-dihydro-1,2,4,3-triazaphospholo[4,5-*a*]quinolines (**1–5**), have been studied as mediators in the electrochemical reduction of 1,1-dichloro-2-methoxycarbonyl-2-methylcyclopropane (DCCP), whose behavior in analogous processes was studied in detail.^{3–6}

Compounds **1–5** undergo stepwise reduction in DMF with 0.1 M Bu₄Nl as supporting electrolyte (Table 1). The coordination number of phosphorus has no effect on the shape of voltammograms. In the first stage, a reversible electron transfer occurs with the formation of unstable radical anions, which is indicated by reduced values of the relative anodic current of the oxidation of radical anions i_{an}/i_{cat} obtained by commutation polarography (see Table 1). The first reduction waves of compounds **1–5** are in the same potential range as those of quinoline and its hydrazino derivatives (compounds **6–8**, Table 1) and, hence, the largest contribution to the HOMO energy creates the hydrazinoquinoline (amidrazone) fragment. Nevertheless, substituents at the phosphorus atom have a pronounced effect on the $E_{1/2}$ reduction potential. For instance, the diethylamino

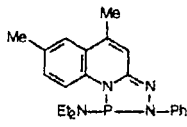
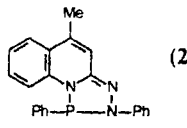
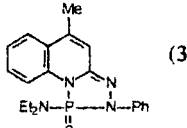

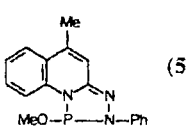
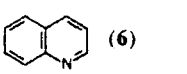
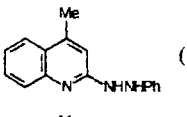
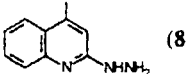
group, which possesses pronounced electron-donating properties, appreciably shifts the reduction potential towards more cathodic values.

Addition of DCCP ($E_{1/2} = -2.07$ V) to solutions of quinolines **1–3** in DMF causes a substantial increase in the limiting currents of the first reduction waves of compounds **1–3** (Table 2). In the case of compound **1**, for which the largest increase in the current is observed, the wave height increases by a factor of 29. Apparently, catalytic reduction of DCCP by organic mediator (**A**) occurs in this case.



The effective rate constants k_{ef} for homogeneous reduction of DCCP with radical anions of quinolines **1–3**, calculated using the Mairanovskii–Benderskii formula,¹ are listed in Table 2. For comparison, the rate constants obtained earlier for other organic electron carriers^{3–6} are also listed in this Table. In the absence of DCCP, radical anions of compounds **1–3** enter into other reactions; therefore, the k_{ef} values (see Table 2) can be considered as minimum ones, reflecting the kinetics of the process only to a first approximation. The actual rates of the process are somewhat higher. The k_{ef} values obtained indicate that the triazaphospholo[4,5-*a*]quinolines studied are highly efficient

Table 1. Electrochemical characteristics of reduction and oxidation waves for 1,2,4,3-triazaphospholo[4,5-*a*]quinolines

| Compound | Reduction | | | Oxidation | | |
|---|----------------|------|------------------|-----------|------|----------------------|
| | $-E_{1/2}/V^a$ | n | i_{an}/i_{cat} | E_p/V^b | n | i_p^{cat}/i_p^{an} |
|  (1) | 1.80 | 1.0 | 0.33 | 0.25 | 0.7 | 0.75 |
| | 2.28 | 2.0 | 0 | 0.77 | 0.8 | 0.70 |
| | | | | 1.29 | 1.1 | 0 |
|  (2) | 1.64 | 1.1 | 0.39 | 0.34 | 0.5 | 0.35 |
| | 2.04 | 1.5 | 0 | 0.86 | 0.8 | 0 |
| | | | | 1.24 | 1.08 | 0 |
|  (3) | 1.58 | 1.0 | 0.14 | 0.67 | 0.5 | 0.75 |
| | 1.97 | 0.7 | 0 | 1.24 | 1.0 | 0 |
| | | | | | | |
|  (4) | 1.75 | 0.71 | 0.32 | 0.30 | 0.5 | 0.75 |
| | 2.07 | 1.20 | 0 | 0.73 | 0.6 | 0.43 |
| | | | | 1.32 | 1.1 | 0 |
|  (5) | 1.78 | 1.0 | 0.30 | 0.53 | 0.6 | 0.15 |
| | 2.07 | 1.3 | 0 | 0.85 | 0.7 | 0 |
| | 2.37 | 2.5 | 0 | | | |
|  (6) | 1.58 | 1.0 | 0.65 | | | |
| | 2.05 | 1.0 | 0 | | | |
| | | | | | | |
|  (7) | 1.18 | 0.4 | 0 | 0.14 | 0.2 | 0 |
| | 1.50 | 0.6 | 0 | 0.78 | 0.3 | 0 |
| | 1.94 | 1.6 | 0 | 0.97 | 0.3 | 0 |
|  (8) | 1.57 | 0.9 | 0 | 0.67 | 0.3 | 0 |
| | 1.73 | 1.5 | 0 | 0.42 | 1.16 | 0 |
| | | | | | | |

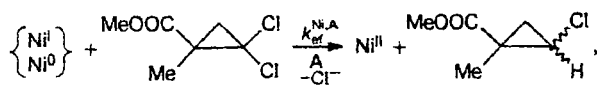
Note: n is the number of electrons; E_p is the peak potential.

^a In DMF/0.1 M Bu₄Nl vs. Hg/I⁻.

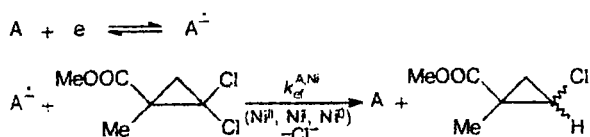
^b In MeCN vs. Ag/0.01 M AgNO₃ in MeCN.

carriers of electrons to the molecule of the given substrate. The efficiency of these electron carriers is even somewhat higher than that of known mediators. The reductive ability of radical anions of compounds 1–3 regularly increases as their reduction potentials increase.

Triazaphospholo[4,5-*a*]quinolines 1–3 were also studied as components of double mediator systems with Ni^{II} ions used in the electrochemical reduction of DCCP. In this case the action of organic mediators (A) as cocatalysts of the substrate reduction with nickel ions was evaluated by the increase in the limiting current of the reduction wave of the metal ion ($k_{ef}^{Ni,A}$)



while the action of metal ions as cocatalysts was evaluated by increase in the first reduction wave of the organic electron carrier ($k_{ef}^{A,Ni}$)



The k_{ef} values obtained are listed in Table 3. In the absence of an organic electron carrier, Ni^{II} ions at

Table 2. Effective rate constants for homogeneous reduction of 1,1-dichloro-2-methoxycarbonyl-2-methylcyclopropane by 1,2-dihydro-1,2,4,3-triazaphospholo[4,5-*a*]quinoline radical anions in DMF^a

| Compound | $-E_{1/2}/V^b$ | i_{cat}/i_d^c | $k_{ef}/L \text{ mol}^{-1} \text{ s}^{-1}$ |
|--------------------------------|----------------|-----------------|--|
| 1 | 1.80 | 29.5 | 106000 |
| 2 | 1.64 | 7.1 | 6070 |
| 3 | 1.58 | 1.6 | 220 |
| Pyrene ^d | 1.55 | 2.1 | 460 |
| 2-Aminoanthracene ^d | 1.55 | 2.0 | 370 |
| Anthracene ^d | 1.44 | 1.3 | 100 |

^a Conditions: at 25 °C, with 0.1 M Bu₄Nl as supporting electrolyte, $C_A = 1 \cdot 10^{-3} \text{ mol L}^{-1}$, $C_{DCCP} = 2.5 \cdot 10^{-2} \text{ mol L}^{-1}$. The ratio of commutated anodic current to the cathodic current for reversible processes under these conditions ($f = 10 \text{ Hz}$, $t_1 = 0.5 \text{ s}$) is 0.7.

^b Potentials of the first reduction wave of triazaphospholo[4,5-*a*]quinolines at a dropping mercury electrode vs. Hg/|I⁻.

^c The ratio of limiting currents of the first wave of the reduction of triazaphospholo[4,5-*a*]quinolines in the absence (i_d) and in the presence of 2-methyl-2-methoxycarbonyl-1,1-dichlorocyclopropane (i_{cat}).

^d Data taken from Ref. 5.

potentials equal to their reduction potentials virtually do not catalyze the reduction of DCCP. In the presence of triazaphospholo[4,5-*a*]quinolines, DCCP is rather efficiently reduced with the nickel ions in a low or in zero oxidation state. In this case the efficiency of the mediator system depends on the metal ion : organic electron carrier ratio. For the studied range of $C_{Ni} : C_A$ ratios, the system with a $C_{Ni} : C_A$ ratio of 2 : 1 was found to be the most efficient. At other ratios (1 : 1 or 1 : 2) the efficiency of the catalytic system decreases. Triazaphospholo[4,5-*a*]quinolines are not reduced at potentials equal to the reduction potentials of the metal ion ($E_{1/2} = -0.6$ to -0.7 V) and likely act only as ligands together with nickel ions.

At potentials equal to the generation potentials of radical anions of triazaphospholo[4,5-*a*]quinolines, the organic electron carrier—metal ion system can be already considered as a double mediator system. Catalytic activity of this system is also dependent on the nature of the organic electron carrier and the ratio of the two mediators. In the case of the most efficient mediator 1, admixture of Ni^{II} salts has virtually no effect on the kinetics of homogeneous reduction of DCCP with radical anions of 1. In the case of compound 3, the admixture of Ni^{II} salts appreciably increases the rate of homogeneous reduction of DCCP; however, this increase is dependent on the concentration of Ni^{II} ions (Table 3).

Thus, the results obtained show that triazaphospholo[4,5-*a*]quinolines are highly efficient in the mediator and double mediator electrochemical reduction of DCCP. Oxidation of compounds 1–3 occurs at low

Table 3. Effective rate constants for electrochemical reduction of 1,1-dichloro-2-methoxycarbonyl-2-methylcyclopropane in the presence of the double mediator system 1,2-dihydro-1,2,4,3-triazaphospholo[4,5-*a*]quinoline—Ni^{II} ions in DMF

| Organic electron carrier | $C_A \cdot 10^3$ mol L ⁻¹ | $C_{Ni} \cdot 10^3$ mol L ⁻¹ | $k_{ef}^{Ni,A}$ L mol ⁻¹ s ⁻¹ | $k_{ef}^{A,Ni}$ L mol ⁻¹ s ⁻¹ |
|--------------------------|---|--|--|--|
| 1 | 1.0 | 1.0 | 150 | 105000 |
| | 2.0 | 1.0 | 70 | 42000 |
| 2 | 1.0 | 1.0 | 90 | 220 |
| | 1.0 | 2.0 | 20000 | 33400 |
| | 2.0 | 1.0 | 400 | 480 |
| | 4.0 | 1.0 | ≤20 | 150 |
| 3 | 1.0 | 1.0 | ≤20 | 26600 |
| | 1.0 | 2.0 | 630 | 22000 |
| | 2.0 | 1.0 | 510 | 7300 |

Note. With 0.1 M Bu₄Nl as supporting electrolyte, at 25 °C, $C_{DCCP} = 5 \cdot 10^{-2} \text{ mol L}^{-1}$.

potentials (see Table 1) with the formation of radical cations,⁹ which also indicates the possibility of using them as mild mediators in the electrochemical oxidation of organic compounds.

Experimental

Electrochemical reduction of triazaphospholo[4,5-*a*]quinolines 1–5 obtained according to the known procedures^{7,8} and the kinetics of homogeneous reduction of DCCP were studied by polarography in DMF with 0.1 M Bu₄Nl as supporting electrolyte. Purification of the solvent and supporting electrolyte, polarographic measurements, and calculations of kinetic parameters were carried out according to the previously described procedures.^{3–6} The capillary characteristics were: $m = 0.71 \text{ mg s}^{-1}$ and $t = 0.5 \text{ s}$. A mercury pool (-0.5 V vs. s.c.e.) served as reference electrode, the commutation frequency was 10 Hz, and the temperature was 25 °C. The solution was deaerated with argon. Electrochemical oxidation was studied by cyclic voltammetry using a PI-50-1 potentiostat in acetonitrile with 0.1 M Et₄NClO₄ as supporting electrolyte. A glassy-carbon disk electrode ($d = 2 \text{ mm}$) pressed into fluoroplastic served as working electrode; an Ag/0.01 M AgNO₃ electrode in MeCN with a potential of +0.3 V vs. s.c.e. served as reference electrode with Pt wire as auxiliary electrode. The potential scan rate was 0.1 V s⁻¹.

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