

Study of the catalytic activity of electrochemically reduced forms of phthalocyanines in the reaction of CO₂ with epoxides

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Catalytic activity of electrochemically reduced forms of mono- and diphthalocyanine complexes of transition and rare-earth elements in the reaction of carbon dioxide with epoxides is considerably higher than that of corresponding neutral forms. The catalytic efficiency depends on the nature of the phthalocyanine complex, the method of the catalyst immobilization, and the electrophilicity of epoxide.

Key words: mono- and diphthalocyanines, lanthanides, rare-earth elements, catalysis, electrochemistry.

It is known that the reactivity of metallocomplexes can be substantially enhanced by the transfer of an electron to the LUMO of the complex or by elimination of an electron from its HOMO.^{1–3} Such an activation can be performed chemically (*i.e.*, using reducing or oxidizing agents), electrochemically, or photochemically.⁴ Different types of reactions catalyzed by electron transfer are known for organic complexes of transition metals; these are first of all ligand exchange,^{1,2,5} *cis–trans*- and haptotropic isomerizations,^{1,5,6} insertion or extrusion of CO and CO₂,^{1,3} *S_{RN}1* reactions,^{7–10} and some other reactions.

The lifetime of species formed in this case is an important factor determining the possibility for the process catalyzed by electron transfer to occur. It must be comparable with the rate of the reaction performed. In other words, the reduction (or oxidation) of metallocomplex, as applied to the electrochemical activation, must be reversible in the time scale of the reaction in question. This restriction is often of crucial importance, in particular for compounds containing a carbon–metal σ -bond.⁸

Phthalocyanine complexes of transition and rare-earth elements (REE) are convenient systems for performing reactions catalyzed by electron transfer. They are reversibly reduced and oxidized and, moreover, they often are capable of undergoing several reversible redox transitions in accessible potential range.¹¹ A rich redox chemistry of this class of compounds causes their wide use as catalysts, *e.g.*, in the oxidation of alkenes and arenes,^{12–14} carbonyl compounds,^{15,16} in reactions of isomerization¹⁷ and reduction of organic compounds,^{18,19}

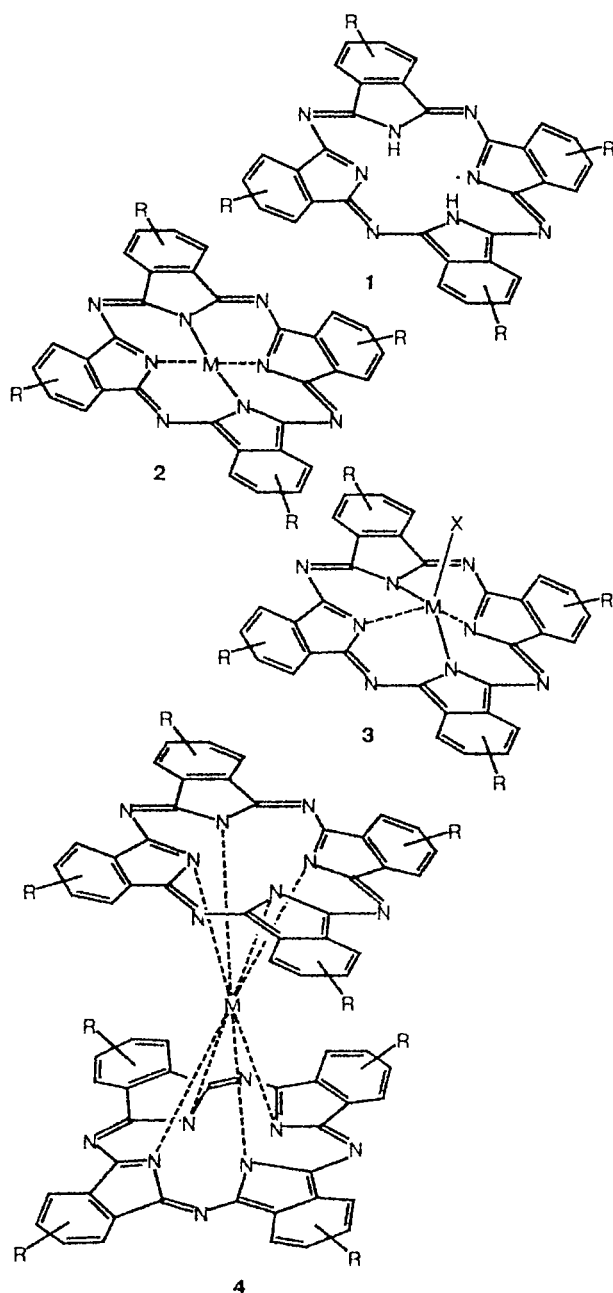
and many other reactions (see review²⁰ and references cited therein).

Recently,²¹ it has been shown that mono- and diphthalocyanine complexes of certain transition and rare-earth elements can serve as catalysts in the reaction of carbon dioxide with epoxides resulting in the formation of cyclic alkylene carbonates. However, these reactions occur under severe conditions. It can be assumed that the reduced forms of phthalocyanines will be more efficient catalysts of this reaction and make it possible to perform it under milder conditions. The aim of this work was to study the catalytic activity of electrochemically reduced forms of mono- and diphthalocyanine complexes of transition and rare-earth elements in the reaction of CO₂ with epoxides.

Results and Discussion

To study the catalytic activity of electrochemically reduced forms of phthalocyanines (**1**), we chose tetra-*tert*-butyl-substituted phthalocyanines (Pc^t) of the Group VIII elements, Pd and Rh (complexes of these elements are well known as highly efficient catalysts of various reactions), and a series of diphthalocyanine complexes of REE, whose catalytic activity has virtually not been studied. The nature of the metal in diphthalocyanine REE complexes (**2–4**) was varied in such a way that compounds containing early, medium, and late REE could be considered.

Structure **1** contains no metal; complexes **2** and **3** (X is an axial ligand) are phthalocyanines containing diva-



R = H, Bu^t

lent and trivalent metals, respectively, and 4 are diphthalocyanines of REE.

Electrochemical potentials of redox transitions of phthalocyanine complexes

To study the catalytic activity of the reduced forms of the above complexes, the potentials at which their redox transitions occur should be known.

Table 1. Potentials of redox transitions of phthalocyanine complexes

Compo- und	$E^{\text{red}}/\text{V}^a$				E^{ox}/V^b		
	E_1^{red}	E_2^{red}	E_3^{red}	E_4^{red}	E_1^{ox}	E_2^{ox}	E_3^{ox}
Pc ^t ₂ Lu ^c	0.02	-1.10	-1.45	-1.87	0.35	1.52	1.70
Pc ^t ₂ Pr	0.19	-1.11	-1.42	-1.81	0.51	1.40	
Pc ₂ Dy	0.20	-0.95	-1.38	-1.63	0.53	1.05	
Pc ₂ Lu	0.14	-1.02	-1.37	-1.71	0.53	1.11	1.60
Pc ^t Pd	-0.82	-1.21			0.79		
Pc ^t RhCl ^c	-0.88	-1.29	-1.52	-1.85	0.81	1.45	

Note. Experimental conditions: $C = 5 \cdot 10^{-4}$ mol L⁻¹, MeCN, or a CH₂Cl₂—MeCN mixture (1 : 4), Pt, 0.05 M Bu₄NBF₄, Ag/AgCl/KCl, 200 mV s⁻¹, 20 °C.

^a Potentials of reduction peaks.

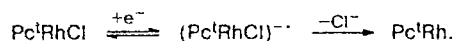
^b Potentials of oxidation peaks.

^c In pure MeCN, other — in MeCN—CH₂Cl₂ mixture.

Previously,²² only the first potential of oxidation of the complex Pc^tPd (0.718 V, vs. SCE) at the Pt electrode in a nitrobenzene—benzophenone (4 : 1) mixture was known. Because of the poor choice of the solvent (the cathodic region appears to be almost inaccessible), the authors of Ref. 22 failed to study the whole series of successive redox transitions. It should be noted that the low solubility of phthalocyanine complexes of various metals often makes their investigation and practical use difficult. Though the substitution of protons by *tert*-butyl radical in the benzene rings of the phthalocyanine ligand appreciably increases the solubility of metal complexes in organic solvents commonly used in electrochemical studies, it often remains poor.

To study the redox properties of the above complexes, we chose a MeCN—CH₂Cl₂ mixture (4 : 1 by volume). The use of this mixture makes it possible to extend considerably the range of accessible potentials to both anodic and cathodic regions. The measurements were carried out with Pt electrodes by cyclic voltammetry (CV) and by the rotating disk electrode (RDE) methods using 0.05 M Bu₄NBF₄ as supporting electrolyte. The potentials obtained are listed in Table 1.

Previously,²³ the potentials of the first oxidation and first reduction peaks of complex Pc^tRhCl measured in DMF were known. Using the MeCN—CH₂Cl₂ system, we succeeded in determining the potentials of six redox transitions (two anodic and four cathodic processes) for this complex. Unlike Pc^tPd, the transfer of the first electron occurs irreversibly and results in cleavage of the Rh—Cl bond, though this process is not very fast in the CV time scale and at high rates of the potential scan (500 mV s⁻¹) it is possible to observe a low inverse peak of (Pc^tRhCl)^{-•} oxidation:

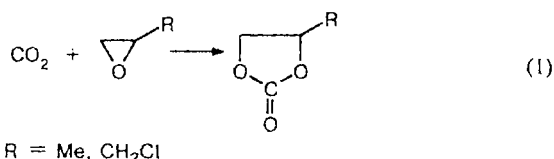


Previously,²⁴ we performed a detailed study of electrochemical properties of the diphthalocyanine complexes of REE in a wide range of potentials. The poten-

tials of redox transitions for these complexes are also listed in Table 1.

Catalytic activity of reduced forms of phthalocyanines

The aim of this work was to compare the catalytic activity of neutral, mono-, and direduced forms of mono- and diphtalocyanines and free $\text{Pc}^{\text{I}}\text{H}_2$ using the interaction of carbon dioxide with epoxides as model reaction.



In the absence of catalyst, CO_2 reacts neither with propylene oxide nor with epichlorohydrin. Addition of free $\text{Pc}^{\text{I}}\text{H}_2$ to the reaction mixture also does not result in the formation of alkylene carbonates. Among phthalocyanines studied previously,²¹ $\text{Pc}^{\text{I}}\text{AlCl}$ appeared to be the most efficient catalyst of the reaction of CO_2 with epoxide; however, high temperature (180 °C) and a pressure of 50 atm are required for the process to occur. The phthalocyanines $\text{Pc}^{\text{I}}\text{RhCl}$ and $\text{Pc}^{\text{I}}\text{Pd}$ have not been studied,²¹ while diphtalocyanines of REE appeared to be much less efficient catalysts (even under such severe conditions, the yields of alkylene carbonates hardly reached 10%).

Data of preparative-scale electrolysis. The results of preparative-scale electrolysis showed that in the electrochemically reduced form each of the phthalocyanine compounds studied catalyzes the reaction of CO_2 with epoxides with the formation of cyclic alkylene carbonates (reaction (1)) under mild conditions (at room temperature and at atmospheric pressure).

The GLC-MS analysis of the reaction mixtures indicates that in all cases the main product of reactions with propylene oxide was propylene carbonate, whereas in the case of reactions with epichlorohydrin the main product was α -chloromethylethylene carbonate. The formation of these compounds was also confirmed by IR spectroscopy. The positions of the characteristic bands of the reaction products, propylene carbonate and α -chloromethylethylene carbonate, completely coincided with those of the pure specimens ($\nu(\text{CO})$ at 1794 cm^{-1} and at 1809 cm^{-1} , respectively).

In addition to the main product, propylene carbonate ($\nu(\text{CO})$ at 1794 cm^{-1}), the formation of acyclic ester $\text{HC}(\text{O})-\text{O}-\text{CH}_2-\text{CHRO}^-\text{Bu}_4\text{N}^+$ ($\nu(\text{CO})$ at 1723 cm^{-1}) was observed in the reaction with propylene oxide.

Virtually no formation of acyclic esters occurs when using a stronger electrophile, epichlorohydrin, as a "trap" of activated CO_2 .

We studied the effect of various factors on the turnover number under given conditions. This value can serve

as an adequate characteristic of the yield of the reaction product, alkylene carbonate. The amount of alkylene carbonate formed in solution was evaluated using a curve of the dependence of the intensity of the $\nu(\text{CO})$ absorption band on the concentration of alkylene carbonate in solution plotted using IR spectroscopy data.

The data listed below illustrate the comparative influence of various factors on the turnover number of the studied reaction (1):

Potentials applied

Reduction potential	Pc_2Lu	Pc_2Pr	$\text{Pc}^{\text{I}}\text{Pd}$	$\text{Pc}^{\text{I}}\text{RhCl}$	$\text{Pc}^{\text{I}}\text{H}_2$
First	125	93	250	52	480
Second	360	585	305	342	530

Procedure for introducing the catalyst into reaction

Type of catalyst	$\text{Pc}^{\text{I}}\text{Pd}$	$\text{Pc}^{\text{I}}\text{RhCl}$	$\text{Pc}^{\text{I}}\text{H}_2$	Pc_2Pr
In solution	20	10	10	25
Immobilized on graphite	250	52	530	585

Duration of the reaction with epichlorohydrin

τ/min	Pc_2Pr	$\text{Pc}^{\text{I}}\text{H}_2$ (graphite rod)	$\text{Pc}^{\text{I}}\text{H}_2$ (porous graphite)
75	350	325	2000
150	585	530	3500

The nature of epoxide (with Pc_2Pr as catalyst)

Propylene oxide	Epichlorohydrin
140	585

The nature of catalyst (10^{-6} mol L^{-1} , graphite, 1 mL of epichlorohydrin, at a potential of the first reduction wave, $\tau = 150$ min)

Pc_2Lu	Pc_2Lu	Pc_2Pr	Pc_2Dy	$\text{Pc}^{\text{I}}\text{Pd}$	$\text{Pc}^{\text{I}}\text{RhCl}$	$\text{Pc}^{\text{I}}\text{H}_2$
125	92	93	90	250	52	480

CV data. It is of interest to compare the data of preparative-scale electrolysis and the results obtained by cyclic voltammetry.

A comparison of the voltammetric picture observed in argon and in carbon dioxide can serve as a criterion for potential electrochemical activity of the complexes under study toward the CO_2 molecule. For instance, it has been shown²⁵ that bubbling CO_2 through a PcCo solution causes a catalytically induced increase in the current of the second reduction wave of PcCo , which indicates that an electron is transferred from the species formed to the CO_2 molecule.

We compared cyclic voltammograms of various phthalocyanine complexes and metal-free $\text{Pc}^{\text{I}}\text{H}_2$ obtained in argon atmosphere and when bubbling CO_2 through the solution and in all cases did observe the catalytically induced increase in the current in CO_2 atmosphere. The difference was only on which of the reduction waves of the compounds studied electrocatalysis occurred. The cyclic voltammograms of $5 \cdot 10^{-4}$ M solutions of Pc_2Lu in MeCN in argon atmosphere and in CO_2 are shown in Fig. 1. As can be seen, the current of the first reduction

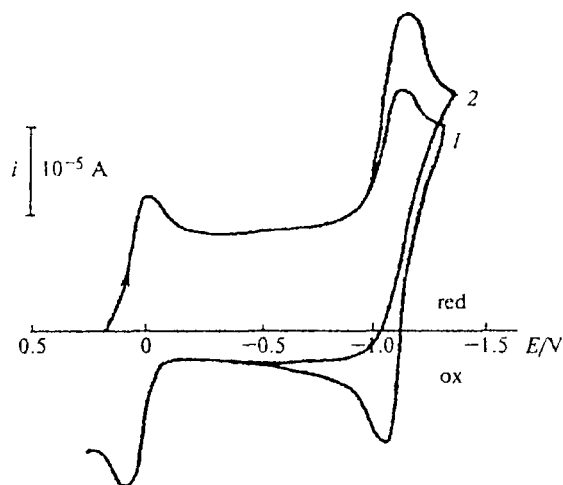
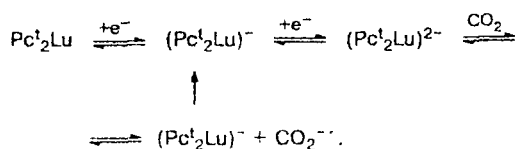


Fig. 1. Cyclic voltammograms of $5 \cdot 10^{-4}$ M solutions of Pc_2Lu in MeCN (Pt, 0.05 M Bu_4NBF_4 , vs. Ag/AgCl/KCl) in argon (1) and in CO_2 (2).

wave remains unchanged, whereas the current of the second wave of the complex reduction increases followed by loss of its reversibility when bubbling CO_2 .

A similar voltammetric picture is characteristic of mediator electrocatalytic process, the general scheme of which, as applied to Pc_2Lu , looks as follows:



The loss of reversibility of the second reduction peak is explained by the fact that the $(\text{Pc}_2\text{Lu})^{2-}$ dianion formed loses its electron to the CO_2 molecule rather than to the electrode (as in argon atmosphere and to which the inverse oxidation peak corresponds) to be converted into anion that is immediately converted into dianion at a given potential (resulting in increase in the current), *etc.* It should be noted that the oxidation waves of Pc_2Lu in argon atmosphere and in CO_2 are identical. This indicates that only doubly reduced forms of Pc_2Lu are electrochemically active toward CO_2 . A voltammogram obtained after cessation of CO_2 bubbling through the solution followed by blowing it with argon recovers its initial shape.

A similar picture was observed for the Pc_2Dy , Pc_2Pr , and Pc_2Lu complexes, as well as for Pc^1H_2 : an increase in the current of the second reduction wave in the presence of CO_2 was observed in all cases. However, in the case of Pc^1Pd bubbling CO_2 results in an increase in current of the first wave of the complex reduction followed by the loss of its reversibility. For Pc^1RhCl , the picture is less pronounced (since the first reduction wave is not completely reversible); however, one can con-

Table 2. Values of currents (10^{-5} A) of the cathodic waves of phthalocyanines in argon (I_{Ar}) and in carbon dioxide (I_{CO_2})

Compound	$I_{\text{CO}_2}/I_{\text{Ar}}$ at E_1^{red}	$I_{\text{CO}_2}/I_{\text{Ar}}$ at E_2^{red}
Pc^1H_2	1.0 ^a	1.6 ^b
Pc^1Pd	3.0 ^b	1.0 ^a
Pc^1RhCl	1.2 ^b	2.1 ^b
Pc_3Lu	1.0 ^a	1.4 ^b
Pc_2Lu	1.0 ^a	1.5 ^b
Pc_2Pr	1.0 ^a	1.6 ^b
Pc_2Dy	1.0 ^a	1.4 ^b

Note. Electrolysis conditions: Pt, MeCN- CH_2Cl_2 , 0.05 M Bu_4NBF_4 , 200 mV s^{-1} ; E_1^{red} and E_2^{red} are the first and the second reduction potentials, respectively.

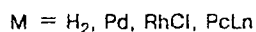
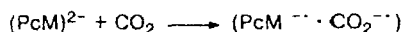
^a Reversibility retains.

^b Loss of reversibility.

clude that the currents of the first two reduction waves increase. The data compared are listed in Table 2.

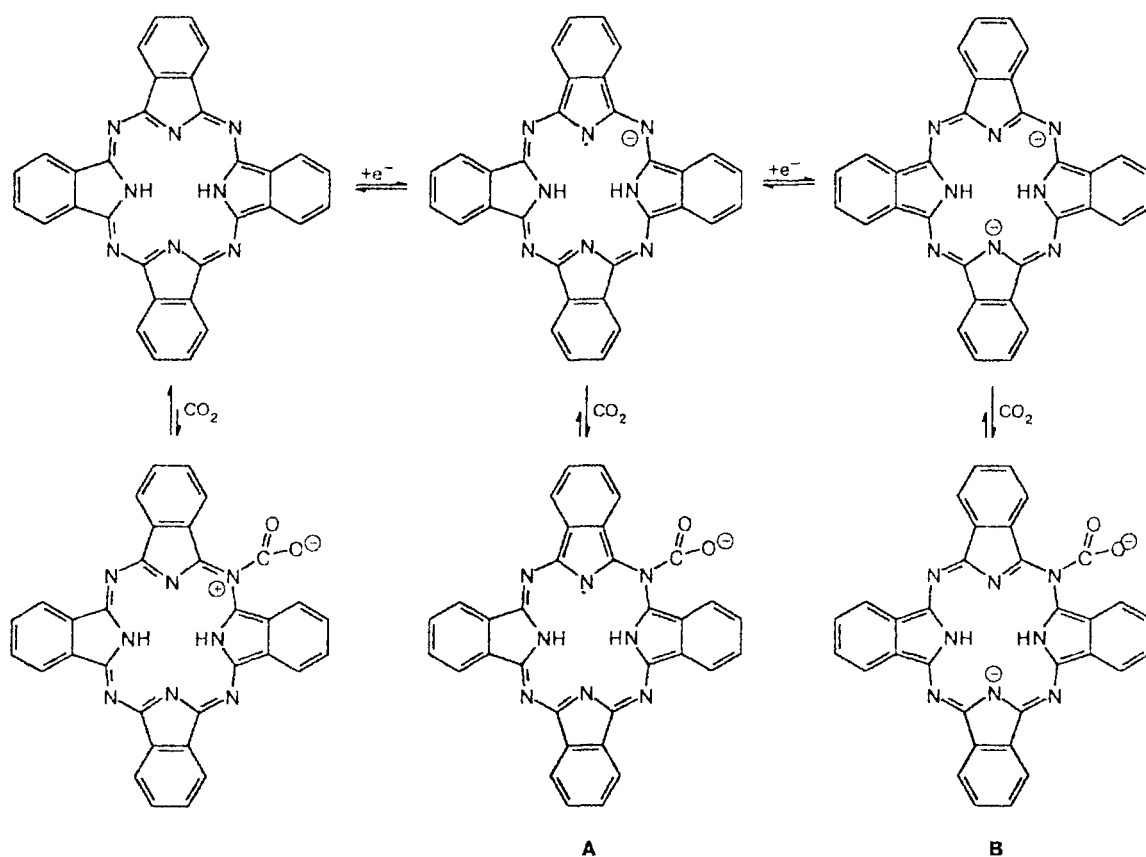
Proposed mechanism of catalytic process. The results of preparative-scale electrolysis of the mixtures containing phthalocyanine, epoxide, and CO_2 showed that the reactions occur not only at those potentials at which catalytically induced increase in the current of the complex reduction in the presence of CO_2 is observed (this would be not surprising), but also at the potentials of the first reduction waves of Pc^1H_2 and diphthalocyanine complexes of Lu, Dy, and Pr. Thus, it can be assumed that the mechanisms of the catalytic action of mono- and dianionic forms of the phthalocyanines studied (except for Pc^1Pd) are different.

It is known that electrocatalytic reduction of CO_2 with phthalocyanine complexes of transition metals can occur in the potential range from -1.2 to -1.7 V and that the reaction products are dependent on the composition of the solution and the metal nature.²⁶ The CV data (see Fig. 1 and Table 2) indicate that electrocatalytic reduction of CO_2 also occurs in the systems under consideration at potentials of the second reduction waves of the complexes (for Pc^1Pd , this process occurs at a potential of the first reduction wave).



The potentials of the first reduction waves of diphthalocyanines and Pc^1H_2 (0.1 ± 0.1 V and -0.70 V, respectively) are too low (in absolute values), therefore it will be difficult to perform the catalytic electroreduction of CO_2 . It is most likely that in this case the monoanionic form of phthalocyanine catalyzes a conventional chemical reaction of CO_2 with epoxides rather than an electrochemical reaction. Since the reduced forms of both diphthalocyanines and Pc^1H_2 are catalytically active, it is logical to assume that the phthalocyanine ring plays a key role in this process. However, the unreduced Pc^1H_2

Scheme 1



does not catalyze the reactions of CO_2 with epoxides. It is known²⁷ that in PcH_2 and PcM the LUMO are localized on the nitrogen atoms of the phthalocyanine ring, hence it is on these atoms that the electron density increases upon reduction. It can be assumed that the CO_2 molecule will be coordinated to the site on which the maximum electron density is localized to form an anion similar to the carbamic acid anion. As is known, carbamic acids exist as salts since the free acids are unstable at room temperature and immediately decompose into CO_2 and amine.²⁸

Analogously, the equilibrium of the reaction with CO_2 will be shifted to the left, toward the initial compound when using neutral PcH_2 . In the case of mono- or dianionic forms of phthalocyanine, the adduct formed will be much more stable, since the fragment with the negative charge on the nitrogen atom is a bad leaving group. The foregoing can be illustrated by Scheme 1 (for simplicity, only one resonance form for each species is shown).

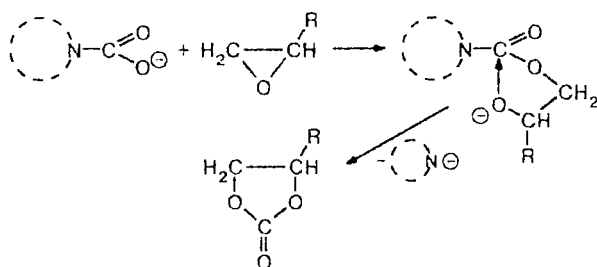
In the diphthalocyanine complexes of trivalent metals considered, the LUMO are also localized on the nitrogen atoms of the phthalocyanine ring,²⁹ therefore two equal rings (each with a charge of 2^-) are formed in

their one-electron reduction (from the classical viewpoint, in the unreduced form the charge of one Pc ring is 2^- , whereas that of the other Pc ring is 1^-). The coordination of CO_2 molecule to the electrochemically reduced phthalocyanine ring of the diphthalocyanine complex will result in the formation of an anion similar to **B** (see Scheme 1), which should also be relatively stable.

The reactions of reduced forms of phthalocyanines with CO_2 are accompanied by changes in the IR spectra, which can be considered taking $\text{Pc}_2\text{Lu}^{3-}$ as an example. A band at 1640 cm^{-1} appears in the $\text{Pc}_2\text{Lu}^{3-}$ spectrum when bubbling CO_2 and disappears after reaction with electrophile, e.g., propylene oxide. This is likely associated with the formation of a carbamate type anion,³⁰ as is shown in Scheme 1. Typical changes are also observed in the far IR spectra (see below).

In the presence of electrophile, e.g., α -alkylene oxide, the adduct of phthalocyanine with the CO_2 formed nucleophilically opens the epoxide ring and the alkoxide ion formed replaces the phthalocyanine, which is a weaker base because of delocalization of the negative charge over the whole long conjugation chain. In this case the reaction proceeds as shown in Scheme 2.

Scheme 2



As can be seen, the active form of the catalyst is regenerated in the course of reaction. According to the proposed scheme, the reaction occurs at the phthalocyanine ring and the role played by the metal atom is that:

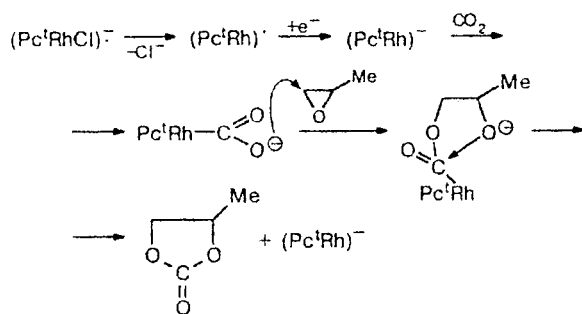
(1) it substantially decreases the reduction potential of the system (-0.70 V for $\text{Pc}^{\text{I}}\text{H}_2$ vs. $+0.19$ V for $\text{Pc}^{\text{I}}_2\text{Pr}$) and, hence, favors the increase in the reaction selectivity, since the reagents (CO_2 traps) present in solution will not be reduced;

(2) it favors delocalization of the negative charge on the phthalocyanine ring, thus making a better leaving group;

(3) coordination to the metal atom "stacks" the two phthalocyanine rings one above the other, due to which charge transfer from one ring to the other ring becomes possible.

However, for monophthalocyanine complexes in which the metal atom is not "sandwiched" between two phthalocyanine rings, the reaction with CO_2 can occur at the metal center (Scheme 3).

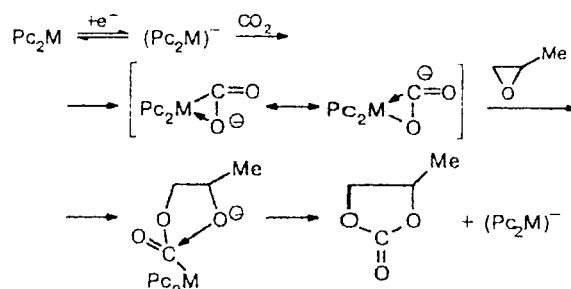
Scheme 3



In our opinion, the reactions of diphthalocyanine complexes at the metal atom are less probable; at the same time, it is known³¹ that REE are capable of increasing their coordination numbers from 4 to 12 (Scheme 4).

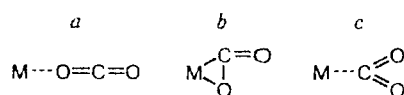
Computer calculations. To evaluate the possibility of CO_2 coordination to the metal atom of sandwich diphthalocyanine molecules, we calculated the geometry, electron density distribution, electrostatic potential, and orbit energies of a model molecule, yttrium

Scheme 4



diphthalocyanine Pc_2Y . Yttrium is similar in properties to lanthanides, therefore it is often used instead of lanthanides when performing theoretical calculations.

Three possible types of CO_2 bonding to the central metal atom of the diphthalocyanine (Fig. 2) complex were considered:



For any type of bonding, the $\text{M}-\text{O}$ and $\text{M}-\text{C}$ bond lengths are close (~ 2.3 Å). Coordination of CO_2 to Y results in distortion of the phthalocyanine rings so that the distance between them (the perpendicular passing through the carbon atom of the CO_2 molecule) increases from 3.05 to 5.24 Å (type a), 5.27 Å (type b), and 5.37 Å (type c).

Though the necessity of such a strong distortion of the geometry of the initial Pc_2Y molecule upon coordination to CO_2 does not rule out the possibility of forming the complexes shown above, it produces some kinetic hindrances to the penetration of CO_2 molecule into the inter-ring space.

Far IR absorption spectra of phthalocyanines. The spectroscopic study of the reaction mixtures included recording and analyzing the IR spectra of initial rhodium and palladium phthalocyanines, lutetium and praseodymium diphthalocyanines, and the spectra of their electrochemically reduced forms both in the presence and in the absence of CO_2 in the spectral region from 4000 to 100 cm^{-1} . It should be noted that only near and medium vibrational IR spectra of these compounds are known to date,³² whereas the far IR spectra (in the region from 600 to 100 cm^{-1}) have not been studied. The far IR spectra of compounds studied contain a rather large number of bands due to both vibrations of the macrocycle and those of the metal-ligand bond (Table 3). In our opinion, it is surprising that after reduction of all the compounds under study and bubbling CO_2 , their far IR absorption spectra became virtually identical. As can be seen from the data in Table 3, a very intense band in the region 520 cm^{-1} and a broad band near 380 cm^{-1} are observed in the

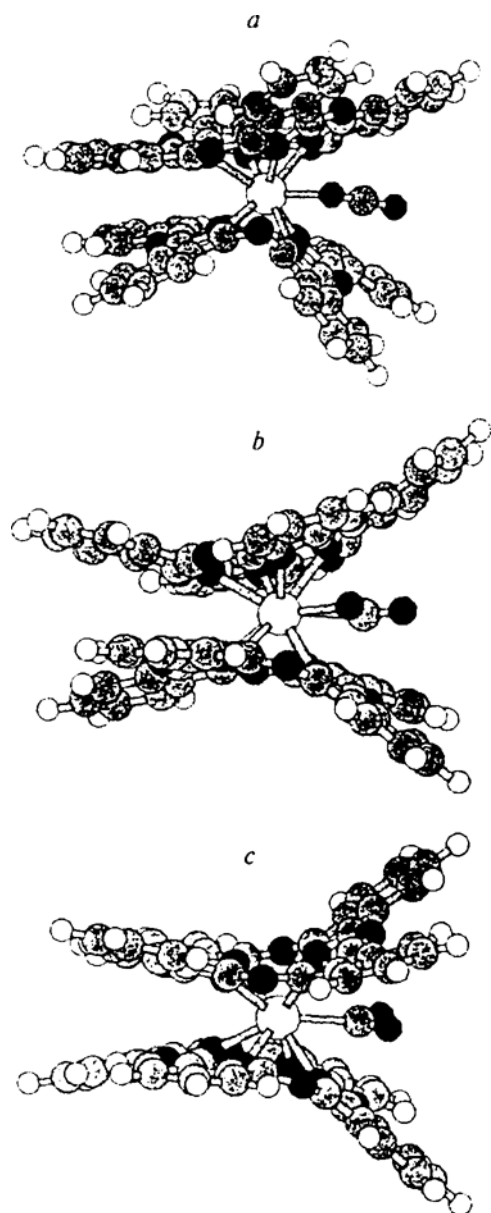


Fig. 2. Optimal structures of $\text{Pc}_2\text{Y}-\text{CO}_2$ complexes with CO_2 coordination to the metal atom calculated by the method of molecular mechanics MM+. Types of coordination: *a*, to oxygen atom; *b*, to both O and C atoms; and *c*, to carbon atom.

IR spectra. Currently, we have no explanation for this experimental fact.

Data of CV and preparative-scale electrolysis indicate that the electrochemically reduced forms of mono- and diphthalocyanine complexes of transition and rare-earth elements and the metal-free $\text{Pc}^{\text{I}}\text{H}_2$ can serve as catalysts

Table 3. Positions of absorption bands in the far IR (the region $600-100\text{ cm}^{-1}$) spectra of phthalocyanines and products of their reduction in CO_2 atmosphere (polyethylene films)

Compound, system	ν/cm^{-1}
$\text{Pc}^{\text{I}}\text{H}_2$	600 w, 564 w, 523 w, 494 v.w, 444 w, 328 w
$\text{Pc}^{\text{I}}_2\text{Lu}$	568 w, 528 v.s, 477 w, 465 v.w, 416 w, 377 w, 247 w, 188 m, 153 m
$\text{Pc}^{\text{I}}_2\text{Pr}$	568 m, 556 w, 530 sh, 522 s, 503 v.s, 443 m, 366 w, 327 w, 265 m, 253 m, 142 m
$\text{Pc}^{\text{I}}_2\text{RhCl}$	590 w, 565 m, 535 m, 526 s, 519 sh, 499 w, 447 m
$\text{Pc}^{\text{I}}\text{H}_2^{\cdot-} + \text{CO}_2$	564 v.w, 521 v.s, 484 v.w, 393 v.s.br
$[\text{Pc}^{\text{I}}_2\text{Lu}]^{\cdot-}$	564 v.w, 528 sh, 520 vs, 479 v.w, 379 m, 352 w
$[\text{Pc}^{\text{I}}_2\text{Lu}]^{\cdot-} + \text{CO}_2$	564 v.w, 528 sh, 520 v.s, 479 v.w, 379 m, 352w
$[\text{Pc}^{\text{I}}_2\text{Pr}]^{\cdot-} + \text{CO}_2$	520 v.s, 390 w.br
$[\text{Pc}^{\text{I}}_2\text{RhCl}]^{\cdot-} + \text{CO}_2$	521 v.s, 383 v.s.br

of the reaction of CO_2 with epoxides. The proposed procedure for electrochemical activation of the catalyst to fix carbon dioxide has some advantages. First, it is possible to convert CO_2 into valuable organic substances, alkylene carbonates, rather than into the usual products of its electrocatalytic reduction (CO , HCOOH , and CH_4). Alkylene carbonates are monomers used in fine organic synthesis and can be converted into environmentally safe polymeric products that remove CO_2 from its cycle in nature for long. Attempts to obtain such a result under mild conditions have failed thus far. Second, in the case of diphthalocyanines it is possible to carry out the reaction at uniquely low potentials (-0.1 V vs. Ag/AgCl). It should be emphasized that the process occurring in this case is a chemical reaction of CO_2 with epoxide catalyzed by the monoreduced form of diphthalocyanine rather than an electrocatalytic reduction of CO_2 . Because of the fact that the electrochemical reduction of diphthalocyanines of rare-earth elements occurs readily, it is possible to achieve high selectivity of the process, since no side reactions of electroreduction of other electrochemically active compounds present in solution occur.

The turnover number and, hence, the yield of alkylene carbonate are dependent on the strength of electrophile (CO_2 trap). Epichlorohydrin, which is a stronger electrophile, appeared to be more efficient than propylene oxide.

Since no consumption and decomposition of the catalyst occurs in the course of the reaction, the increase in the turnover number per mole of the catalyst can be achieved simply by increasing duration of the reaction.

A procedure used for introducing the catalyst into the reaction is also important. Catalyst immobilized on

a graphite electrode appears to be more efficient than that present in solution. Probably, this is due to higher local concentration of the reagents in the vicinity of the surface of the graphite electrode than in the case of carrying out the reaction in solution, since the CO_2 solubility in the $\text{MeCN}-\text{CH}_2\text{Cl}_2$ (4 : 1) mixture used is rather low. It should be noted that the yield of the reaction product is strongly dependent on the graphite structure and porosity.

Experimental

Instruments and electrodes. The electrochemical oxidation and reduction potentials were measured on a PI-50 potentiostat at a stationary and rotating disk Pt electrodes of diameter 5.14 mm in anhydrous MeCN and CH_2Cl_2 using Bu_4NBF_4 as supporting electrolyte at 20 °C. The potential scan rate was varied from 50 to 500 mV s^{-1} .

The preparative-scale electrochemical production of reduced forms of phthalocyanines was carried out using a P-5827M potentiostat in the potentiostat regime in a specially constructed electrolytic cell with separated anodic and cathodic compartments at Pt and graphite electrodes in an anhydrous MeCN or $\text{MeCN}-\text{CH}_2\text{Cl}_2$ mixture of various compositions (depending on the phthalocyanine solubility) using Bu_4NBF_4 as supporting electrolyte at 20 °C. The course of electrolysis in solution was monitored in accordance with the change in the electrolysis current. When the residual current was not more than 10% of its initial value, the electrolysis was stopped. Spectroelectrochemical data served as an additional criterion for the formation of mono- or dianionic form in solution. The electronic spectra of the solutions obtained coincided with the reported data. In all cases, a saturated silver-chloride electrode was used as reference electrode.

The absorption spectra were recorded on a Specord UV-spectrometer in the region 270–900 nm. IR spectra were recorded on Nicolet Magna 750 and Bruker-IFS 25 Fourier spectrometers in the region 100–4000 cm^{-1} as CaF_2 films and in CaF_2 cuvettes ($d = 0.024$ mm) with a resolution of 2 cm^{-1} .

GLC-MS spectra were recorded on a Varian MAT-442 mass spectrometer (70 eV).

Computer calculations were carried out by the method of molecular mechanics (MM+, geometry calculations) and semiempirical ZINDO/1 method incorporated into the HYPERCHEM (Release 4) program. The correctness of calculations of the diphtalocyanine geometries was tested by calculating the molecule of metal-free phthalocyanine and comparing the results obtained with the data of X-ray study. It turned out that the results obtained from ZINDO/1 and MM+ calculations are in good agreement with the data of X-ray study. Further, the geometry of yttrium complexes and their adducts with CO_2 was calculated by the MM+ method.

Solvents. Acetonitrile of "pure" grade was stirred for 24 h over CaH_2 and filtered, and then KNO_3 (5 g) and conc. H_2SO_4 (10 mL) was added to 1 L of the solvent. The mixture was refluxed for 3 h and distilled, then MeCN was refluxed for 2 h over P_2O_5 and distilled again; b.p. 81–83 °C.

Methylene chloride of "pure" grade was refluxed for 2 h over CaH_2 and stored over CaH_2 . Freshly distilled CH_2Cl_2 was used in the experiments.

Gases. Argon from a cylinder was passed through a column filled with anhydron. Gas supplied into the cell was saturated with solvent vapors in an additional vessel.

Carbon dioxide ("special purity" grade) from a cylinder was used without additional purification and saturated with solvent vapors.

Synthesis of initial compounds. The initial phthalocyanine complexes were synthesized following the standard procedures.³³

Reaction of CO_2 with epoxide in the presence of catalytic amounts of reduced forms phthalocyanines (general procedure). Solutions of reduced forms of mono- and diphtalocyanine complexes obtained by potential-controlled electrolysis were used as catalysts in the reaction of CO_2 with epoxides. To this end, a solution of a reduced form, through which CO_2 was preliminarily bubbled for 30 min, was transferred by CO_2 flow into a Schlenk tube containing propylene oxide or epichlorohydrin. Then CO_2 was bubbled through the mixture obtained for 1 h and the vessel was hermetically sealed in CO_2 atmosphere, and stored for further analyzing the reaction products.

If a graphite electrode was used as working electrode, it was preliminarily coated with a catalyst (phthalocyanine complex). Then the electrode was placed into a solution containing a mixture of MeCN, an epoxide, and 0.02 M Bu_4NBF_4 . Argon and then CO_2 was bubbled through the solution for 15 min. Then the desired potential was set using the potentiostat and the cell was switched on. Electrolysis was performed with continuous CO_2 bubbling. After electrolysis, the solution was transferred from the electrochemical cell by CO_2 flow into a Schlenk tube preliminarily blown with CO_2 , hermetically sealed in CO_2 back flow, and stored for analyzing the reaction products.

The concentrations of alkylene carbonates formed were determined using IR spectroscopy data. To plot the curves of the dependences of the area of characteristic bands of α -chloromethylethylene carbonate ($\nu(\text{CO})$ at 1809 cm^{-1}) and propylene carbonate ($\nu(\text{CO})$ at 1794 cm^{-1}) on the molar concentration of standard solutions, IR spectra of solutions with the known concentrations were recorded in CaF_2 cell of thickness 0.024 mm.

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