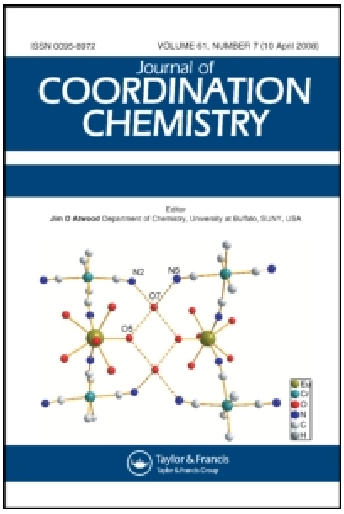


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Theoretical study of the electron transfer reaction of hydrazine with cobalt(II) phthalocyanine and substituted cobalt(II) phthalocyanines

Diego A. Venegas-Yazigi[a]; Gloria I. Cárdenas-Jirón[b]; José H. Zagal[b]
[a] Departamento de Química, Facultad de Ciencias Naturales, Matemáticas y del Medio Ambiente, Universidad Tecnológica Metropolitana, Ñuñoa, Santiago, Chile [b] Departamento de Ciencias Químicas and Departamento de Química de los Materiales, Facultad de Química y Biología, Universidad de Santiago de Chile, Santiago, Chile

To cite this Article Venegas-Yazigi, Diego A. , Cárdenas-Jirón, Gloria I. and Zagal, José H.(2003) 'Theoretical study of the electron transfer reaction of hydrazine with cobalt(II) phthalocyanine and substituted cobalt(II) phthalocyanines', Journal of Coordination Chemistry, 56: 14, 1269 — 1275

To link to this Article: DOI: 10.1080/00958970310001624267

URL: http://dx.doi.org/10.1080/00958970310001624267

J. Coord. Chem., Vol. 56, No. 14, 20 September 2003, pp. 1269–1275

Taylor & Francis
Taylor & Francis Group

THEORETICAL STUDY OF THE ELECTRON TRANSFER REACTION OF HYDRAZINE WITH COBALT(II) PHTHALOCYANINE AND SUBSTITUTED COBALT(II) PHTHALOCYANINES

DIEGO A. VENEGAS-YAZIGI[a,]*, GLORIA I. CÁRDENAS-JIRÓN[b,]*
and JOSÉ H. ZAGAL[b]

[a]*Departamento de Química, Facultad de Ciencias Naturales, Matemáticas y del Medio Ambiente, Universidad Tecnológica Metropolitana, Av. J. P. Alessandri 1242 , Ñuñoa, Santiago, Chile;*
[b]*Departamento de Ciencias Químicas and Departamento de Química de los Materiales, Facultad de Química y Biología, Universidad de Santiago de Chile, Casilla 40, Correo 33, Santiago, Chile*

(Received 31 December 2002; In final form 25 August 2003)

A theoretical model is proposed to explain the trend in reactivity of cobalt(II) phthalocyanine (CoPc) and substituted cobalt(II) phthalocyanines for the oxidation of hydrazine. Our study suggests that the reaction occurs via a *through bond charge transfer* pathway and not *via* a *through space charge transfer* pathway as was shown in previous work for the oxidation of 2-mercaptoethanol by CoPc (G.I. Cárdenas-Jirón and D.A. Venegas-Yazigi, *J. Phys. Chem. A.* **106**, 11398 (2002)). We propose a mechanism for the oxidation of hydrazine based on a four-step energy profile which agrees with a mechanism proposed for the electro-oxidation of hydrazine mediated by cobalt phthalocyanines confined on a graphite electrode. We show that the step in the energy profile that involves formation of a radical of hydrazine seems to be a good starting point for the study of the transfer of the first electron in the oxidation of hydrazine mediated by different substituted cobalt(II) phthalocyanines.

Keywords: Redox reaction; Cobalt phthalocyanine; Oxidation of hydrazine; Energy profile; Electron transfer

INTRODUCTION

Metallophthalocyanines are well known as catalysts for a great variety of electrode reactions [1, 2]. When incorporated on electrode surfaces they act as mediators for many reactions, providing sites for the molecules to interact, thus lowering the activation energy. This is reflected in the lowering of the overpotential for a given reaction compared with the unmodified electrode. Correlations have been found [1–10] between the activity of these complexes measured through the rate constant and their redox potential. In fact 'tuning' the redox potential of these complexes by changing the metal or changing the substituents on the periphery of the phthalocyanine ligand has

---

*Corresponding authors. E-mail: dvy@manquehue.net; gcardena@lauca.usach.cl

ISSN 0095-8972 print: ISSN 1029-0389 online
DOI: 10.1080/00958970310001624267

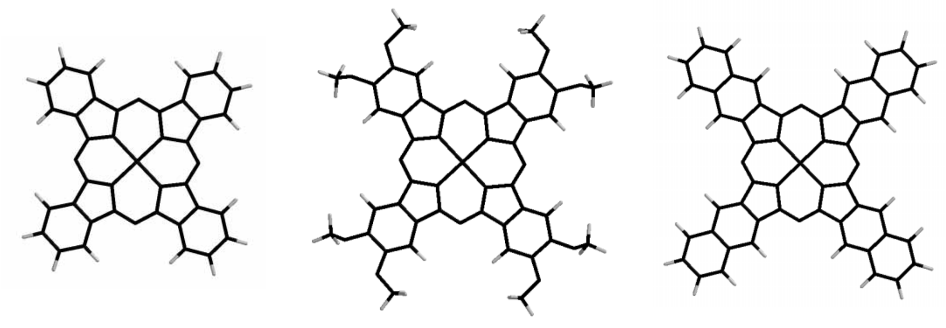
been suggested as a strategy for optimizing their activity for a particular reaction [2]. In many metallophthalocyanines the redox potential reflects an electron transfer process involving the metal center [1, 2] which is usually the active site that interacts with the incoming molecule, facilitating the electron transfer process between the electrode and the interacting molecule *via* the metallophthalocyanine. The Co(II)/(I) redox potential of cobalt phthalocyanines (CoPcs) can be correlated with the frontier orbital energies such as highest occupied molecular orbital (HOMO) for an oxidation process and lowest unoccupied molecular orbital (LUMO) for a reduction process in a closed-shell system. In previous work using PM3(tm) semiempirical calculations we have found linear correlations between the energy of the HOMO located on the Co and the Co(II)/(I) redox potential [11].

We are particularly interested in finding correlations between theoretical parameters and experimental results to predict reactivities. For example, we have shown that the calculated donor–acceptor intermolecular hardness (η_{DA}) [12–14], as a reactivity descriptor, correlates very well with the experimental rate constant values (k) measured for the electroreduction of molecular oxygen mediated by CoPc and substituted CoPcs [15,16]. We also found good correlations between k and η_{DA} values for the electro-oxidation of 2-mercaptoethanol (2ME) by CoPc and substituted CoPcs [15,17]. Inclusion of a graphite cluster in the theoretical study of the interaction of CoPc and 2ME has been examined and its effect produces a decrease in the activation energy for bond formation between both molecules [18]. On the other hand, we characterized the global reactivity of transition metal macrocycles using the molecular hardness, chemical potential, electrophilicity and the local reactivity using the Fukui function and the electrostatic potential giving good agreement between the reactivity of the systems and basic reactivity principles such as hard soft acid base (HSAB) [19, 20]. As we found in previous work the oxidation reaction of 2ME mediated by CoPc occurs *via* a *through space charge transfer* mechanism [21], we are interested in finding a possible mechanism governing the early stages of the oxidation reaction of hydrazine mediated by CoPc. From the point of view of the calculation level, we have found that the PM3(tm) semiempirical method gives good results at a low computational cost for these large systems [15–19,21].

THEORETICAL AND COMPUTATIONAL DETAILS

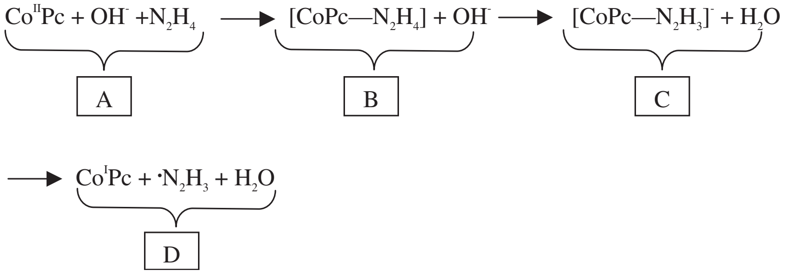
We performed SCF/MO semiempirical calculations using a UHF procedure for open-shell systems and an RHF procedure for closed-shell systems. A PM3 Hamiltonian parameterized for transition metals provided by the TITAN package called PM3(tm) was used [22]. The studied molecules are cobalt(II) phthalocyanine (CoPc), cobalt(II) octamethoxyphthalocyanine (CoMeOPc) and cobalt(II) 2,3-naphthalocyanine (CoNPc) which are shown in Fig. 1.

In the first stage we studied the interaction between CoPc and hydrazine along a reaction coordinate defined by the distance between the cobalt atom and one of the nitrogen atoms of hydrazine (N_2H_4) ($r_{Co\cdots N}$). We optimized the molecular geometry for the whole CoPc$\cdots N_2H_4$ structure constraining the distance between the cobalt atom and the donor atom of the substrate (N). The studied distances were 3.0, 4.0, 5.0 and 6.0 Å. In the second stage we studied the interaction between CoPc and N_2H_4 at the equilibrium distance between both molecules with a full geometry optimization.



(a) (b) (c)

FIGURE 1 Structural view of the (a) CoPc, (b) CoMeOPc and (c) CoNPc molecules.



SCHEME 1

In the last stage, we build the energy profile for CoPc and substituted CoPc (CoMeOPc and CoNPc) according to Scheme 1 proposed previously [23].

In the next section we use Scheme 1 and verify the validity of this mechanism on the basis of reactivity trends found with these CoPcs [23].

RESULTS AND DISCUSSION

Charge Transfer: Through Space or Through Bond

In previous work we suggested that, for the interaction between CoPc and 2ME, charge transfer occurs through space (TSCT) [21]. In that work, we found that local properties such as spin density (ρ_x^s) and atomic net charge (q_x) are very good charge transfer descriptors (CTDs). The values of these two properties change dramatically from 5.0 to 4.8 Å along the reaction coordinate defined as the distance between the cobalt atom of CoPc and the sulfur atom of 2ME. Between 3.8 and 4.8 Å the values of the CTDs remain almost constant which corresponds to the region where the CT occurs [21]. Analogously, we did several theoretical calculations for the $CoPc\cdots N_2H_4$ system along the coordinate defined as the distance between the cobalt atom of CoPc and the nitrogen atom of N_2H_4 ($r_{Co\cdots N}$). Table I summarizes the results obtained for

TABLE I Calculated values for the spin density (ρ_x^s) and atomic net charge (q_x) for the CoPc···N_2H_4 system at four different $r_{Co\cdots N}$ distances

CoPc···N_2H_4	*3.0* Å	*4.0* Å	*5.0* Å	*6.0* Å
q_{Co}	−0.2941	−0.3281	−0.2923	−0.2927
q_N	−0.0195	−0.0733	−0.0770	−0.0773
ρ_{Co}^s	−0.3638	−0.2680	−0.3164	−0.3062
ρ_N^s	0.0030	1.60×10^{-5}	4.40×10^{-4}	5.00×10^{-6}

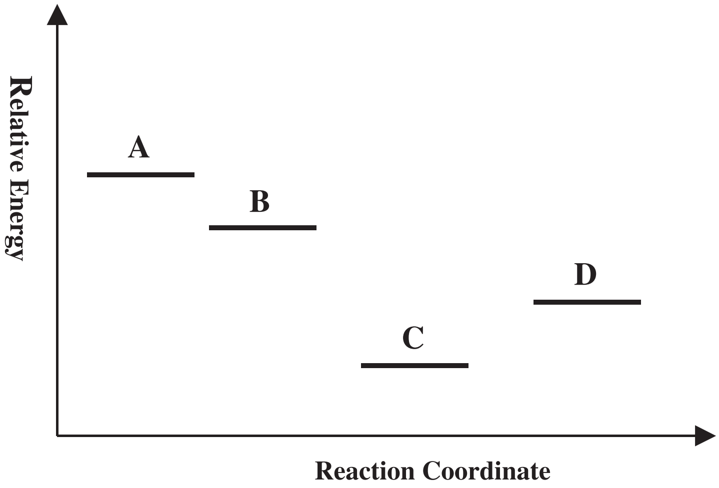


FIGURE 2 Relative energy profile for the interaction of CoPc with hydrazine.

the CTDs (ρ_x^s and q_x) for the CoPc...N_2H_4 system at $r_{Co\cdots N} = 3.0$, 4.0, 5.0 and 6.0 Å. No changes were observed for both CTDs. Therefore, the CT is not occurring through space as with the redox reaction of CoPc and 2ME [21].

Previous studies using electron paramagnetic resonance spectroscopy [24] suggest that oxidation of hydrazine involves the initial formation of a 1:1 adduct between a Co(II)TSPc (cobalt(II)tetrasulfophthalocyanine) and hydrazine. On the other hand, a mechanism for the electro-oxidation of hydrazine by CoPc and substituted CoPc (CoPcX, where X represents the substituent on the periphery of the phthalocyanine ligand) has been suggested as presented in theoretical and computational details [23].

On the basis of this information, we follow a charge transfer through bond (TBCT) pathway which was built following Scheme 1. We calculate the bonded CoPcX–N_2H_4 and $[CoPcX–N_2H_3]^-$ adduct systems for the B and C steps, respectively, to build an energy profile characterizing the electron transfer reaction which is presented in Fig. 2 (X = naphtho, methoxy). As an illustration, we present in Fig. 2 the energy profile corresponding to the interaction of CoPc with hydrazine. Table II shows the results of the relative total energies calculated for each of the four steps described in Scheme 1 for each complex, CoPc, CoNPc and CoMeOPc, reacting with hydrazine. For each of the three systems formation of an adduct between CoPcX and N_2H_4 (step B) involves a higher stabilization than the isolated species (step A), as expected. Following Scheme 1, the loss of a proton from the bonded adduct CoPcX–N_2H_4 leads to formation of an anionic species (step C) which is lower in energy than the systems involved in steps

TABLE II Calculated relative energy values in eV for the four-step energy profile

System	*A*	*B*	*C*	*D*	ΔE_{CD}
CoPc	0.0000	−3.6061	−8.3730	−4.2022	4.1707
CoNPc	0.0000	−3.6485	−8.0948	−3.9315	4.1633
CoMeOPc	0.0000	−3.6004	−8.9402	−4.3507	4.5895

A and B. The homolytic rupture of the anionic bonded adduct ($[\mathrm{CoPcX{-}N_2H_3}]^-$), step D, leads to an increase in the calculated total energy. Obviously, a radical species is less stable than a non-radical species which explains why the system involved in step D is more unstable than the system involved in step C. In the case of the electrochemical oxidation of hydrazine mediated by CoPcs, the driving force for radical formation is supplied by the externally applied potential to the CoPc–graphite modified electrode and, in the case of the aerobic oxidation of hydrazine catalyzed by cobalt tetrasulfophthalocyanine, the driving force is provided by the oxidation power of oxygen [24]. The oxidation of hydrazine to molecular nitrogen involves a four-electron transfer process. In the reaction coordinate shown in Fig. 2 we have modeled the first electron transfer leading to a radical hydrazine ($^\bullet N_2H_3$) and a $\mathrm{Co^IPcX}$ species (step D). We also show that the precursor species for the first electron transfer corresponds to an anionic bonded species like $[\mathrm{CoPc{-}N_2H_3}]^-$ and not to a neutral bonded species like $\mathrm{CoPcX{-}N_2H_4}$. We conclude that the proposed scheme provides a reasonable mechanism to account for the transfer of the first electron from hydrazine to the CoPc or substituted CoPcs.

Relative Reactivity

As discussed above, the increase in energy produced from steps C to D (ΔE_{CD}) results from the formation of the very unstable $^\bullet N_2H_3$ radical. So the formation of this species is energetically unfavorable and it requires some driving force for the reactions to proceed; this driving force can be externally applied potential [23] or the presence of an oxidizing molecule such as molecular oxygen [24]. The ΔE_{CD} values for the three studied systems are presented in Table II. The order of the ΔE_{CD} values is

$$\mathrm{CoMeOPc} > \mathrm{CoPc} > \mathrm{CoNPc}.$$

For the proposed mechanism, defined as Through Space TSCT or TBCT, the larger ΔE_{CD} value for the CoMeOPc system implies that formation of the $^\bullet N_2H_3$ radical is less favorable with respect to the CoNPc system. The CoPc system presents an intermediate value of ΔE_{CD}. In previous work [23], the trend in reactivities of electrical currents measured at constant potential for the electro-oxidation of hydrazine mediated by CoPc was

$$\mathrm{CoNPc} > \mathrm{CoPc} > \mathrm{CoMeOPc}.$$

Our theoretical results agree with the trend found experimentally, i.e. the CoMeOPc system needs a larger driving force to produce the radical hydrazine and is less reactive to oxidation of hydrazine in the electrochemical oxidation studies [23]. The theoretical results obtained in this work suggest that an energetic component such as ΔE_{CD} could be a good theoretical parameter to rationalize the substituent effect on the oxidation of hydrazine. The results presented in this paper constitute a preliminary study. A larger variety of substituted phthalocyanines are currently under examination.

CONCLUSIONS

We have presented a theoretical model to describe the oxidation of hydrazine with CoPc and substituted CoPcs. From the theoretical results we propose that the first electron transfer process for this reaction should be occurring under a TBCT pathway and not a TSCT pathway as was found in previous work for another oxidation reaction. The obtained energy profile provides a good method to rationalize the oxidation of hydrazine and therefore represents a valid approach to understanding the oxidation of hydrazine. We found that the energy parameter (ΔE_{CD}), which reflects the formation of the hydrazine radical, under our TBCT pathway is a good descriptor to determine the relative trend in reactivity of CoNPc, CoPc and CoMeOPc systems. There is good agreement between the theoretical results of ΔE_{CD} and the trend in reactivity found experimentally for the electro-oxidation of hydrazine mediated by cobalt phthalocyanines confined on a graphite electrode surface.

Acknowledgments

J.H.Z. and G.I.C.-J. would like to acknowledge the financial support from Project FONDECYT Lineas Complementarias No 8010006. G.I.C.-J. also thanks Vicerrectoría de Investigación y Desarrollo (USACH) for a position of Research Associate.

References

[1] J.H. Zagal, *Coord. Chem. Rev.* **119**, 89 (1992).
[2] A.B.P. Lever, *J. Porphyrins Phthalocyanines* **3**, 488 (1999).
[3] F. van der Brink, E. Barendrecht and W. Visscher, *Rec. Trav. Chim. Pays-Bas* **99**, 253 (1980).
[4] P. Vasudevan, H. Santosh, N. Mann and S. Tyagi, *Transit. Met. Chem.* **15**, 81 (1990).
[5] J.P. Randin, *Electrochim. Acta* **19**, 83 (1974).
[6] F. Beck, *J. Appl. Electrochem.* **7**, 191 (1977).
[7] J.A.R. van Veen and C. Visser, *Electrochim. Acta* **24**, 921 (1979).
[8] J.A.R. van Veen, J.F. van Baar, C.J. Kroese, J.G.F. Coolegem and N. de Wit and H.A. Colijn, *Ber. Bunsenges. Phys. Chem.* **85**, 693 (1981).
[9] J.H. Zagal, M. Páez, A.A. Tanaka, J.R. dos Santos and C. Linkous, *J. Electroanal. Chem.* **339**, 13 (1992).
[10] J.H. Zagal, M. Gulppi, M. Isaacs, G. Cárdenas-Jirón and M.J. Aguirre, *Electrochim. Acta* **44**, 1349 (1998).
[11] J.H. Zagal, M. Gulppi and G. Cárdenas-Jirón, *Polyhedron* **19**, 2255 (2000).
[12] R.G. Parr and Z. Zhou, *Acc. Chem. Res.* **26**, 256 (1993).
[13] P.K. Chattaraj, *Proc. Indian Natl. Sci. Acad.* **62A**, 513 (1996).
[14] P.K. Chattaraj, A. Cedillo, E.M. Arnett and R.G. Parr, *J. Org. Chem.* **60**, 4707 (1995).
[15] G.I. Cárdenas-Jirón and J.H. Zagal, *J. Electroanal. Chem.* **497**, 55 (2001).
[16] G.I. Cárdenas-Jirón, M.A. Gulppi, C.A. Caro, R. del Rio, M. Páez and J.H. Zagal, *Electrochim. Acta* **46**, 3227 (2001).
[17] J.H. Zagal, M. Gulppi, C.A. Caro and G. Cárdenas-Jirón, *Electrochem. Commun.* **1**, 389 (1999).
[18] G.I. Cárdenas-Jirón, C.A. Caro, D. Venegas-Yazigi and J.H. Zagal, *J. Mol. Struct.* (*Theochem*) **580**, 193 (2002).

[19] G.I. Cárdenas-Jirón, *J. Phys. Chem. A* **106**, 3202 (2002).
[20] G.I. Cárdenas-Jirón, *Int. J. Quantum Chem.* **91**, 389 (2003).
[21] G.I. Cárdenas-Jirón and D.A. Venegas-Yazigi, *J. Phys. Chem. A* **106**, 11938 (2002).
[22] TITAN 1.0.7, (Wavefunction, Inc. and Schrodinger Inc., 370, Irvine, CA).
[23] D. Geraldo, C. Linares, Y. Chen, S. Ureta-Zañartu and J. Zagal, *Electrochem. Commun.* **4**, 182 (2002).
[24] D.J. Cookson, T.D. Smith, J.F. Boas, P.R. Hicks and J.R. Pilbrow, *J. Chem. Soc. Dalton Trans.* 109 (1977).