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Theoretical Estimation of Charge Transfer Rate at Some Nitrosyl Complexes

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Abstract: The charge transfer at $C_{23}H_{17}F_8N_8O_2PRu$, $C_{44}H_{30}BF_4N_5O_4Ru$, $C_{56}H_{52}CL_5N_5OO_sP_2$ and $C_{76}H_{88}F_{80}N_{24}O_{11}P_{10}Ru_4$ nitrosyl complexes are investigation and studies theoretically using the quantum consideration. Charge transfer behavior largely rely to the electric properties of nitrosyl complexes system whose depending on the main important parameters for the transmission rate constant such that: orientation transition energy, overlapping coupling coefficient, driving force energy, height barrier and Temperature T (K). Data results have been evaluated using a MATLAB program. Results show that rate of charge transfer increases due to increases the orientation transition energy.

Key words: Charge transfer rate, nitrosyl complexes, data, results, important, height barrier

INTRODUCTION

Charge transfer reactions are of fundamental importance to both chemistry and biology. Charge transfer reactions can occur both thermally and photo chemically. In simple terms, an Charge Transfer (CT) reaction involves the transfer of an electron from a 'donor' to an 'acceptor' (Kavarnos, 1993). However, the charge transfer never chemical bonds were broken or reformation and furthermore the changing for the bonding length with angle were smalling (Hussein, 2011). Charge transfer on a molecular level is a very import classes for electron transition reaction that limited ranging from less size of molecule to large complex molecules (Al-Agealy, 2009).

Theory of simple electronic transferring early in 1965 depending on Marcus work. Rudy was describing the transferring interaction due two system; a simple Marcus Model is a good basic of classical transfer theory. Alternatively, the Marcus simple model has been extending to investigation the transferring at system have single donating local state to another accepting continuum state.

The charge transfer field have being and advance due to the detailing by analytical method at past century ago. That's depending on the standard general theory. On the other hand, its introducing new branch technology that's view in photochemical initiation (Al-Aagealy and Hassooni, 2014).

The treatment of electronic transfer due to chemical compound has been focusing due to transfer of charging processes (Gehlen and Chandler, 1992). At charge transition in solvent system in more commonly the charge transfer that considering when a solvent could be rearrangement the all coordinate solvent system and must the system could reorganizes all configuration system and so, the dipole solvent overcharging results to stabilize a negative charge at accepter position. Charge study at transfer in media solvent is very important parameter in research at recently years. Aim of the present research is to calculate the rate of charge transfer at nitrosy complexes $C_{56}H_{52}CL_5N_5OO_sP_2$, $C_{44}H_{30}BF_4N_5O_4Ru$, $C_{23}H_{17}F_8N_8O_2PRu$ and $C_{76}H_{88}F_{80}N_{24}O_{11}P_{10}Ru_4$ using 1-butanol, acetone, methanol, formic acid and DMF solvents.

MATERIALS AND METHODS

Theory: According on the quantum of charge transfer theory, a transfer processes over system contained donor state and acceptor state energies could be treatment non adiabitically transfer at different complex material and the weak interaction at electronic energy levels states due to D-A system. The charge transfer rate of processing from donor to acceptor and must be given a general expression (Al-Agealy and Al-Obaidi, 2009):

$$\Gamma_{ET} = \frac{4\pi^2}{h} \Lambda_{ET}{}^2 FC^{ET} \tag{1}$$

Where:

Λ : The electronic coupling coefficient
FC^{ET} : The nuclear factors are obtained from the density of Franck-Condon states

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The FC^{ET} branch in Eq. 1 is an average factor of Franck-Condon contribution due to acceptor donor system and mathematically the sum due to overlapping over integrals between the wave functions for initial state and final state, respectively with same energy.

The general expression of FC^{ET} is quite estimated depending on temperature T, driving force and orientation transition energy. It is factor takes the simple form (Gao and Marcus, 2000):

$$FC^{ET} = \left(\frac{1}{(4\pi\Delta k_B T)}\right)^{(1/2)} \exp\left[-\frac{(\epsilon+\Delta)^2}{4\Delta k_B T}\right] \tag{2}$$

where, k_B is the Boltzman constant. Substituting Eq. 2 in Eq. 1 results:

$$\Gamma_{ET} = \frac{4\pi^2}{h}\left(\frac{1}{4\pi\Delta k_B T}\right)^{(1/2)} \Lambda_{ET}{}^2 \exp\left[-\frac{(\epsilon+\Delta)^2}{4\Delta k_B T}\right] \tag{3}$$

The orientation transition energy is the sum of both inner and outer (solvent) vibrational modes are included the effect of the polar solvents. The contribution of to the total Δ is given by Hadi *et al.* (2013):

$$\Delta = \frac{e^2}{4\pi\varepsilon_o}\left[\frac{1}{2R_D} + \frac{1}{2R_A} - \frac{1}{R_{DA}}\right]\left[\frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon_s}\right] \tag{4}$$

Where:

ε_o : The vacuum permittivity
ε_s : Constant of static dielectric due to the solvent
ε_{op} : A optical dielectric constant
R_A and R_D : The donor and acceptor radius, respectively
R_{DA} : The sum R_A and R_D

The driving force energy for the charge transfer from donor state. With energy E to the acceptor is related by Wibren (2002):

$$\varepsilon = E - \Delta \tag{5}$$

Where:

$E = h\upsilon$: The absorption energy
υ : The frequency of the spectral
h : The Planck constant

For electron transition the value of radius of the chemical molecules R can be evaluation using spherical approach model:

$$\frac{4\pi}{3}R^3 = \left(\frac{M}{N_A \rho}\right) \tag{6}$$

Where:

M : The molecular weight
ρ : The density of mass
N_A : The Avogadro's number

RESULTS AND DISCUSSION

Quantum quansidaration is have been adapted to evaluation of the rate transition of electron at nitrosyl complexes depending on the estimation of the orientation transition energy Δ, effective energy ∈, the electronic overlapping coupling coefficient ∧ and temperature investigation of electron transition at $C_{23}H_{17}F_8N_8O_2PR$, $C_{44}H_{30}BF_4N_5O_4Ru$, $C_{56}H_{52}CL_5N_5OO_sP_2$ and $C_{76}H_{88}F_{80}N_{24}O_{11}P_{10}Ru_4$, nitrosyl complexes system are depending on the orientation transition energy is the energy required to reorientation of the system before transfer, to initial transfer process. It can be estimated theoretically using the Hush theory using Eq. 4. Radii calculation of for donor state $C_{23}H_{17}F_8N_8O_2PR$, $C_{44}H_{30}BF_4N_5O_4Ru$, $C_{56}H_{52}CL_5N_5OO_sP_2$ and $C_{76}H_{88}F_{80}N_{24}O_{11}P_{10}Ru_4$ and NO for acceptor state using expression in Eq. 6. Inserting the values of molecular weight M and density masses for all nitrosyl complexes from Table 1 in Eq. 6 with we can evaluated the values of radii for all complexes, data results are shown in Table 1.

Depending on radii data result in Table 1, we can be estimation the orientation transition energy for nitrosyl complexes system with solvent in Table 2 using an expression of hush in Eq. 4 depending on MATLAB program, data of the reorientation energies results have been summarized in Table 3 for $C_{23}H_{17}F_8N_8O_2PR$, $C_{44}H_{30}BF_4N_5O_4Ru$, $C_{56}H_{52}CL_5N_5OO_sP_2$ and $C_{76}H_{88}F_{80}N_{24}O_{11}P_{10}Ru_4$ a, respectively.

The transitions of electron Γ_{ET}(1/sec) $C_{23}H_{17}F_8N_8O_2PRu$, $C_{44}H_{30}BF_4N_5O_4Ru$, $C_{56}H_{52}CL_5N_5OO_sP_2$ and $C_{76}H_{88}F_{80}N_{24}O_{11}P_{10}Ru_4$ system can evaluated using Eq. 3 that's a results of quantum postulate.

A MATLAB program used to evaluations the transmission of electron at nitrosyl complexes system with solvent using Eq. 3 and inserting the orientation transition energy Δ(eV) data from Table 3 for $C_{23}H_{17}F_8N_8O_2PRu$, $C_{44}H_{30}BF_4N_5O_4Ru$, $C_{56}H_{52}CL_5N_5OO_sP_2$ and $C_{76}H_{88}F_{80}N_{24}O_{11}P_{10}Ru_4$ system and the overlapping coupling coefficient matrix element $\langle\Lambda_{ET}\rangle = 0.2$ eV (Al-Agealy, 2009). Results data of calculation are listed in Table 4-7 for $C_{23}H_{17}F_8N_8O_2PRu$, $C_{44}H_{30}BF_4N_5O_4Ru$, $C_{56}H_{52}CL_5N_5OO_sP_2$ and $C_{76}H_{88}F_{80}N_{24}O_{11}P_{10}Ru_4$ systems, respectively.

Theoretical evaluation of charge transfer of the chemistry of nitrosyl complexes have attracted increasing attention because of their interesting charge transfer properties, pollution controlling abilities and catalytic functions (Hong *et al.*, 2007). On the other hand the chemistry of Nitrogen monoxide (NO), most commonly referred to as nitric oxide has historically been a topic of great interest to inorganic chemists (Enemark and Feltham, 1974). It is an important in pertinent medical and biosciences research or artificial systems designed for pharmaceutical purposes (Serli *et al.*, 2003). Depending

Table 1: Common properties of nitrosyl complexes (Singh, 2008)

Formula	$C_{56}H_{52}CL_5N_5OO_8P_2$	$C_{44}H_{30}BF_4N_5O_4Ru$	$C_{23}H_{17}F_8N_8O_2PRu$	$C_{76}H_{88}F_{80}N_{24}O_{11}P_{10}Ru_4$	NO
Molecular mass	1240.42	880.61	683.49	3347.52	30.0100
Crystal structure	Monoclinic	Monoclinic	Monoclinic	Monoclinic	
Density (g cm^{-3})	1.519	1.405	1.666	2.035	1.3402
Calculated radius (A)	6.8671	6.2874	5.4591	8.6727	2.0707
Lattice constant (Å)	A = 9.5056, b = 19.4011, c = 14.8581	A = 15.558, b = 15.255, c = 17.567	A = 8.9165, b = 15.8829, c = 19.321	A = 10.9387, b = 26.0442, c = 19.3827	
Electron affinity (eV)	4.0	4.05	4.2 Enemark and Feltham (1974)	4.5 Serli *et al*. (2003)	

Table 2: Common properties of some solvents

Solvent	Chemical formula (David, 2001)	Dielectric constant (Mohr and Taylor, 2000)	Optical dielectric constant
1-butanol	$C_4H_{10}O$	17.84	1.397 Al-Agealy and Hadi (2010)
Aceton	C_3H_6O	21.01	1.356 Al-Agealy *et al*. (2008)
Methanol	CH_4O	33.00	1.329 Al-Agealy and Hadi (2010)
DMF	C_3H_7NO	38.25	1.430 Al-Agealy *et al*. (2008)

Table 3: Data results of the orientation transition energy Δ(eV) for $C_{23}H_{17}F_8N_8O_2PRu$, $C_{44}H_{30}BF_4N_5O_4Ru$, $C_{56}H_{52}CL_5N_5OO_8P_2$ and $C_{76}H_{88}F_{80}N_{24}O_{11}P_{10}Ru_4$ system

Solvent	$C_{23}H_{17}F_8N_8O_2PRu$	$C_{44}H_{30}BF_4N_5O_4Ru$	$C_{58}H_{52}CL_5N_5OO_8P_2$	$C_{76}H_{88}F_{80}N_{24}O_{11}P_{10}Ru_4$
1-butanol	1.31590	1.32310	1.32998	1.35393
Aceton	1.43029	1.43812	1.44559	1.47163
Methanol	1.54522	1.55367	1.56175	1.58988
DMF	1.33376	1.34105	1.34800	1.37230

Table 4: The rate of electron transition Γ_{ET} (1/sec) at $C_{23}H_{17}F_8N_8O_2PRu$ complex

Wave length (nm)	Energy (eV)	1-butanol	Aceton	Methanol	DMF
300	4.1250	4.141×10^{-44}	1.222×10^{-39}	8.236×10^{-36}	2.323×10^{-43}
400	3.0937	1.538×10^{-19}	4.937×10^{-17}	6.913×10^{-15}	4.047×10^{-19}
500	2.4750	3.614×10^{-8}	1.431×10^{-6}	3.335×10^{-5}	6.696×10^{-8}
600	2.0625	5.437×10^{-2}	6.907×10^{-1}	0.6161×10	8.326×10^{-2}
700	1.7678	2.873×10^{2}	1.840×10^{3}	9.004×10^{3}	3.923×10^{2}
800	1.5468	7.557×10^{4}	3.100×10^{5}	1.035×10^{6}	9.576×10^{4}

Table 5: The rate of electron transition Γ_{ET} (1/sec) at $C_{44}H_{30}BF_4N_5O_4Ru$ complex

Wave length(nm)	Energy(eV)	1-butanol	Aceton	Methanol	DMF
300	4.1250	8.346×10^{-44}	2.342×10^{-39}	1.497×10^{-35}	4.636×10^{-43}
400	3.0937	2.279×10^{-19}	7.111×10^{-17}	9.664×10^{-15}	5.962×10^{-19}
500	2.4750	9.643×10^{-8}	1.805×10^{-6}	4.129×10^{-5}	8.571×10^{-8}
600	2.0625	6.465×10^{-2}	8.110×10^{-1}	2.044	9.875×10^{-2}
700	1.7678	3.261×10^{2}	2.069×10^{3}	1.002×10^{4}	4.444×10^{2}
800	1.5468	8.321×10^{4}	3.389×10^{5}	1.124×10^{6}	1.052×10^{5}

Table 6: The rate of electron transition Γ_{ET} (1/sec) at $C_{58}H_{52}CL_5N_5OO_8P_2$ complex

Wave length(nm)	Energy(eV)	1-butanol	Aceton	Methanol	DMF
300	4.1250	1.591×10^{-43}	4.282×10^{-39}	2.631×10^{-35}	8.895×10^{-43}
400	3.0937	3.273×10^{-10}	9.972×10^{-17}	1.325×10^{-14}	8.591×10^{-19}
500	2.475	5.848×10^{-8}	2.239×10^{-6}	5.050×10^{-5}	1.081×10^{-7}
600	2.0625	7.582×10^{-2}	9.413×10^{-1}	0.809×10	1.160×10^{-1}
700	1.7678	3.664×10^{2}	2.306×10^{3}	1.109×10^{4}	4.999×10^{2}
800	1.5468	9.091×10^{4}	3.681×10^{5}	1.214×10^{6}	1.151×10^{5}

Table 7: The rate of electron transition Γ_{ET} (1/sec) at $C_{76}H_{88}F_{80}N_{24}O_{11}P_{10}Ru_4$ complex

Wave length (nm)	Energy (eV)	1-butanol	Aceton	Methanol	DMF
300	4.1250	1.538×10^{-42}	3.431×10^{-38}	1.792×10^{-34}	8.241×10^{-42}
400	3.0937	1.168×10^{-18}	3.202×10^{-16}	3.885×10^{-14}	2.993×10^{-18}
500	2.4750	1.316×10^{-7}	4.711×10^{-6}	1.002×10^{-4}	2.397×10^{-7}
600	2.0625	1.328×10^{-1}	1.573×10^{0}	1.299×10^{1}	2.010×10^{-1}
700	1.7678	5.518×10^{2}	3.356×10^{3}	1.567×10^{4}	7.470×10^{2}
800	1.5468	1.241×10^{5}	4.894×10^{5}	1.568×10^{6}	1.562×10^{5}

on Eq. 3 there are two contributions to the rate, one coming from the Hamiltonian of transition and one from the dissipative one. The physical rate of charge transfer that satisfies the probability of transition at system. In Table 2, we show result of reorientation energy increasing with increasing of polarity term in Eq. 6 that a results of effect both dielectric constant and optical dielectric constant.

Rate of charge transfer increasing with increasing the absorbtion energy that's shown from data in Table 4-7 that's indicate the system have more energy to drive more electron to transfer. The results of rate charge transfer occurs nitrosyl complexes system have large orientation transition energy for all system, for example, $C_{23}H_{17}F_8N_8O_2PRu$ from 8.236×10^{-36} to 1.035×10^6 at $\Delta(eV) = 1.545$ while 4.141×10^{-44} to 7.557×10^4 $\Delta(eV) = 1.31590$ eV at =1.31590 eV.

The weak charge transfer of all nitrosyl complexes in the visible at 300-500 nm are assigned as metal-to-ligand electron transfer and ligand-to-ligand electron transfer to the doubly degenerate here to the excellent π acceptor NO^+, leading to a particular high degree of covalence in that system configuration and thus, to a reluctance in accepting an electron to yield NO. Table 4-7 shows, this effect is.

On the other hands the rate increasing with the solvent more polarity for example, 8.346×10^{-44} to 8.321×10^4 at 1-butanol compare 1.497×10^{-35} to 1.126×10^6 at methanol to more orientation transition energy for complex, this refers to the transfer of electron is more probable in system have more polarity function. Not ably the transition of electronin the system with solvent have large dielectric constant are larger than system with solvent have small dielectric constant that's shown from Table 3-7. Transition rate data for are large for $C_{23}H_{17}F_8N_8O_2PRu$, $C_{44}H_{30}BF_4N_5O_4Ru$, $C_{56}H_{52}CL_5N_5OO_sP_2$ and $C_{76}H_{88}F_{80}N_{24}O_{11}P_{10}Ru_4$ systems with solvent methanol compare with the other solvents, respectively this indicates that there is system with methanol which is more reactive towards charge transfer reaction occurs activity with more polar solvent.

CONCLUSION

Concluding, the present study has demonstrated the applicability of theoretical methodology for the study of relatively simple nitrosyl metal complexes. The effects of charge transfer in these compounds and the electronic structures of the thus, generated species have been investigated. The transition of electron is depending on the orientation transition energy and the driving free energy. Rate of charge transfer increasing with increasing the absorption energy and orientation transition energy and increasing with increasing of polarity term.

However, the transition of electron in the system depending on the solvent type that's indicate the system contain solvent have large dielectric constant are larger than system with solvent have small dielectric constant.

REFERENCES

Al-Aagealy, H.J.M. and M.A. Hassooni, 2014. Effect of semiconductors types on electron transmission at metal/semiconductor interface. J. Chem. Biol. Phys. Sci., 4: 2454-2462.

Al-Agealy, H.J.M. and A.Z. Hadi, 2010. ET between ketone triplets and organic dyes in variety solvent. J. Coll. Basic Educ., 64: 25-36.

Al-Agealy, H.J.M. and R.I.N. Al-Obaidi, 2009. Electron transfer at semiconductor/liquid interfaces. Ibn Al-Haitham J. Pure Applied Sci., Vol. 22, No. 2.

Al-Agealy, H.J.M., 2009. Photo-induced electron transfer between ruthenium (II) tris-(2,2-bipyrdine) and methyl viologen. Ibn Al- Haitham J. Pure Applied Sci., Vol. 22, No. 3.

Al-Agealy, H.J.M., R.I. Al Obaidi and D.F. Alsaaidi, 2008. Effect of solvent types on photo induced electron transfer in methylenblu dye keton. Ibn Al-Haithem J. Pure Applied Sci., 21: 39-49.

David, R.L., 2001. Handbook of Chemistry and Physical. 6th Edn., CRC Press, Boca Raton, Florida, USA.,.

Enemark, J.H. and R.D. Feltham, 1974. Principles of structure, bonding and reactivity for metal nitrosyl complexes. Coord. Chem. Rev., 13: 339-406.

Gao, Y.Q. and R.A. Marcus, 2000. On the theory of electron transfer reactions at semiconductor/liquid interfaces. II. A free electron model. J. Chem. Phys., 113: 6351-6360.

Gehlen, J.N. and D. Chandler, 1992. Quantum theory for free energies of electron transfer. J. Chem. Phys., 97: 4958-4963.

Hadi, J.M., D.S. Shakir and M.A. Hasooni, 2013. Electron transfer between Ruthenium (II)-(trisbipyridine) $Ru(phen)_{3+2}$ and Cobalt (III)-(polypyridyl) $Co(phen)_{3+3}$ at CH_3CN, CH_3OH and Acetone solvents. J. Thi-Qar Sci., 3: 183-189.

Hong, S., T.S. Rahman, K. Jacobi and G. Ertl, 2007. Interaction of NO with $RuO_2(110)$ surface: A first principles study. J. Phys. Chem. C., 111: 12361-12368.

Hussein, K.M., 2011. Study of the electron transfer at metal/semiconductor interface by using quantum mechanical theories. M.Sc. Thesis, University of Baghdad, Baghdad, Iraq.

Kavarnos, G.J., 1993. Fundamentals of Photoinduced Electron Transfer. VCH Publishers, Inc., New York, USA., ISBN: 9780895737519, Pages: 359.

Mohr, P.J. and P. Taylor, 2000. Fundamental physical constant. J. Phys. Chem. Data, l28: 1713-1999.

Serli, B., E. Zangrando, T. Gianferrara, L. Yellowlees and E. Alessio, 2003. Coordination and release of NO by ruthenium-dimethylsulfoxide complexes-implications for antimetastases activity. Coord. Chem. Rev., 245: 73-83.

Singh, P., 2008. The charge transfer Chemistry of nitrosyl complexes. Ph.D. Thesis, Institut Fur Anorganische Chemie Der Universitat Stuttgart, Stuttgart, Germany.

Wibren, D.O., 2002. Charge transfer in blue Coper. Ph.D. Thesis, Debye Institute and University of Utrecht, Utrecht, Netherlands.