

Effect of solvent reorganization on the electron transfer (ET) reaction between donor-acceptor pairs in solution

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Abstract - When a charged or neutral species is in solution, there are always some interactions between the species and its solvation shell in such a way that, at equilibrium conditions, one may consider the solvent cavity as a ligand of a charge transfer complex between the species and its solvent cage. Any charge transfer reaction will be through this specific solvation shell which is assumed to have a fixed coordination and is at equilibrium with the system and is independent of the presence of other reactant species. We will consider first the case where the solvent itself is an acceptor and second, the case where the acceptor is another solute in the same solvent.

Our results indicate that it is the variation of the inner shell solvent reorganization energy (the Marcus λ_{in}) with ΔG° (the standard free energy change for the reaction $A + D \rightarrow A^- + D^+$) which determines the variation of the ET rate constants with ΔG° .

I INTRODUCTION

Intramolecular electron transfer (ET) reactions between donor-acceptor pairs are important steps in many chemical and biological processes. One of the mechanisms that appears to operate in the ET reactions is the charge-transfer (CT) complex models (1-7) which in some case shows features which are sensitive to solvent polarity (2-7). Marcus (3) has been pointing out the important role of the solvent reorganizations on ET reactions between donor-acceptor pairs in solutions and recently we have demonstrated (4) how important is the influence of the inner shell solvent reorganizations (the Marcus λ_{in}) on the variations of outer sphere ET reaction rate constant with ΔG° , the standard free energy change of the ET reaction: $A + D \rightarrow A^- + D^+$.

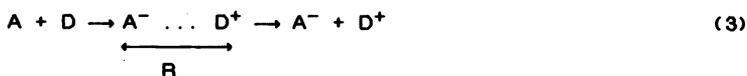
a - We consider that when a charged or neutral species is in solution, there are always some interactions between the species and its solvation shell in such a way that, at equilibrium conditions, one may consider the solvent cavity as a ligand of a charge transfer (CT) complex between the species and its solvent cage:



where ΔH_{CT}^A , ΔH_{CT}^D represent the equilibrium free energy change for solute solvent interactions i.e. the solvent reorganization energy around the solute A or D before the transfer of charge. Depending on ΔH_{CT} value δ can vary from 0 (in non polar solvents) to ≈ 1 . At this state the "solvated species" i has a radius r_i which depends on the properties of that species i (size, force constants of vibrational coordinates in reactions when that species is a reactant and when it is a product) and on its environments (solvent polarity, pH, co-ion size, etc...). Any charge transfer reaction will be through this specific solvation shell which is assumed to have a fixed coordination configuration and is at equilibrium with the system and is independent of the presence of other reactant species.

In this sense, the solvent reorganization energy around the species i , namely ΔH_{CT} may be considered paralleled to the Marcus λ_{in} (eq. 6 in ref. 3).

b - In the process: $A + D \rightarrow A^- + D^+$, we consider further that the reaction proceeds through a solvent shared CT or ion-pair state (4-7).



In this state A^- and D^+ are separated by a distance R and are attracted to each other by a

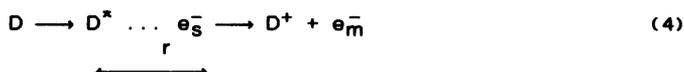
coulombic force $-e^2/RD_s$. Besides, in solution before the reactants are brought to a distance R , each individual reactant i has already obtained a specific inner shell solvent reorganization energy λ_{in}^i which is defined by the species i and by the system in which the species involved is at equilibrium conditions. λ_{in}^i is also independent of other reactant species presence.

c - The solvent is considered as a semiconductor with a large band gap and with a conduction band depth V_0 .

We first consider the case where the acceptor is the solvent itself. Next we will consider the case where the acceptor is another solute in the same solvent.

II CASE WHERE THE SOLVENT IS AN ELECTRON ACCEPTOR: PHOTOIONIZATION OF D

The solute solvent cavity is an electron acceptor. The reduced species A^- is a solvated electron, e_s^- (7) :



where e_m^- is the quasifree electron, i.e., a mobile electron in solution and r is the solvent cavity radius. Upon photoexcitation, the species D^* will enter an intermediate CT or ion pair state where D^* transfers its electron to its solvent cavity. In this activated CT state, the electron is attracted to D^+ by coulomb force, $-e^2/r D_s$ (D_s = the solvent static dielectric constant) at a distance which is the solvent cavity radius of D^* . The photoionization in solution can be considered as a vertical phototransition of a solvated electron into the edge of the solvent conduction band against the electric field of the solute cation D^+ :

$$I_s = E_1 e_s^- + (e^2/r)(1/D_{op} - 1/D_s) + e^2/r D_{op} \quad (5)$$

where $e^2/r(1/D_{op} - 1/D_s)$ is the solvent reorganization $\lambda = \lambda_{in} + \lambda_{out}$ around D , where D is in the ground state, λ_{in} , and when D is in the CT state, λ_{out} . In a homogeneous solvent, the solvent cage has the same constituent as the medium, so that eq 5 becomes eq 6 :

$$I_s = E_1 e_s^- + e^2/r D_{op} \quad (6)$$

Eq 6 permits the calculation of the effective radius of the solvated cation. Recent experimental results in picosecond laser photoexcitation reported by Mataga et al. (8) give strong support for our solute-solvent cage CT model i.e. a cation and a solvated electron ion pair as a precursor state for photoionization.

The I_s is also related to the solute gas phase ionization energy I_g by the relation (7) :

$$I_s = I_g + P_+ + \Delta H_{CT} + V_0 \quad (7)$$

where $P_+ = -(e^2/2r)(1 - 1/D_{op})$ is the polarization energy of D^+ and V_0 , the solvent conduction band depth.

Correlations between I_g , I_s , $E_1 e_s^-$ and $E_{1/2}^{ox}$ (the standard electrochemical oxidation potential of D), E_s^+ , (the solvation energy of D^+). Alternately, D can also be oxidized by electrochemical oxidation technique. In this case, its oxidation potential energy $E_{1/2}^{ox} + E_{re}$ (E_{re} the standard reference electrode potential) is referred to the energy of the quasi free electron in the vacuum level of the solvent conduction band V_0 . Whereas in the photoionization case, the I_s is referred to that of electron in the lowest level of the solvent conduction band. Hence (9) :

$$E_{1/2}^{ox} + E_{re} = I_g + E_s^+ = I_s + V_0 \quad (8a)$$

and for an acceptor :

$$E_{1/2}^{red} + E_{re} = EA - E_s^- = I_s + V_0 \quad (8b)$$

Where EA , E_s^- are the gas phase electron affinity of A and the solvation energy of the anion A^- respectively.

Fig. 1 resumes all the correlations above for a donor case.

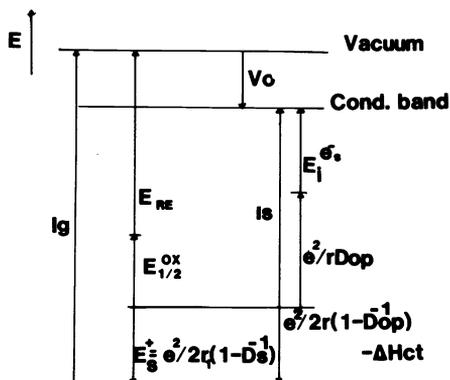


FIG. 1 Position of the electrochemical and photoionization energy level of a solute relative to that of a solvated electron and the vacuum of a non mixed solvent (taken from ref. 10).

Application

Determination of V_0 . Eqs (8a) and (8b) permit to find V_0 once the experimental values of I_S , $E_{1/2}^{ox}$ of the solute are known. This is the first time that V_0 of polar solvents are determined by means of both techniques : electrochemical oxidation and photoionization techniques.

The solvation energy E_S^+ of an ion is composed of a solvent reorientation energy, ΔH_{CT} , around the partially ionized ion before the transfer of charge, plus the electronic polarization, P_+ of the completely oxidized (or reduced) ion during the transfer of charge to the electrode. The electrochemical value of ΔH_{CT} and of P_+ is different from the corresponding value obtained in the photoionization case. However, their sum $\Delta H_{CT} + P_+$ is the same for both experiments. The solvation energy E_S^+ for an ion is found experimentally (9-10) to be :

$$E_S^+ = -e^2/2r(1 - 1/D_S) \quad (9)$$

and at equilibrium conditions :

$$E_S^+ = -e^2/2r(1 - 1/D_S) = -e^2/2r(1-1/D_{Op}) + \Delta H_{CT} \quad (10).$$

Hence we deduced the general equation for $\Delta H_{CT} = \lambda_{in}$:

$$\Delta H_{CT} = \lambda_{in} = -e^2/2r(1/D_{Op} - 1/D_S) \quad (11)$$

Eq. 11 is the general eq. formulating the solvent reorganization energy around a species with a solvation shell of radius r_i . Since r_i is specific for each reactant i (or product), hence λ_{in} is also specific for each reactant i . If the reactant species i is at equilibrium conditions with its surroundings throughout the ET reaction, its cavity radius r_i will be the same in eq. for E_S^+ , P^+ and ΔH_{CT} . If the reactant species is an excited state during the ET reaction, in which case the excited species may not be at equilibrium conditions with its surroundings and thus its solvation shell may be electronically different in the ground and in the excited state. The r_i value hence will differ in eqs. for E_S^+ , P_+ and λ_{in} (11) (for detail, please see ref. 11).

For various solutes in the same solvent, according to fig 1, V_0 and E_S^{\pm} are constant, hence $P_+ = e^2/2r(1 - 1/D_{Op})$ and consequently E_S^+ will vary linearly with I_g or $E_{1/2}^{ox}$ provided ΔH_{CT} is also a linear function of I_g or $E_{1/2}^{ox}$ or is independent of the solvent. Plots of P_+ vs I_g for over 40 aromatic compounds in acetonitrile show indeed a straight line (11). In acetonitrile, $\Delta H_{CT} = -0,5$ eV is independent of the solvent. However, in a more polar solvent such as water, $\Delta H_{CT} = \lambda_{in}$ is found to vary linearly with $\Delta G^* = E_{1/2}^{ox} - E_{1/2}^{red}$ (Fig. 2). One notes that for the donor compounds, λ_{in}^D increases linearly with ΔG^* whereas for the acceptor compounds λ_{in}^A decreases linearly with ΔG^* . As we will see later this observation has an important consequence on the variation of the ET rate constant with ΔG^* .

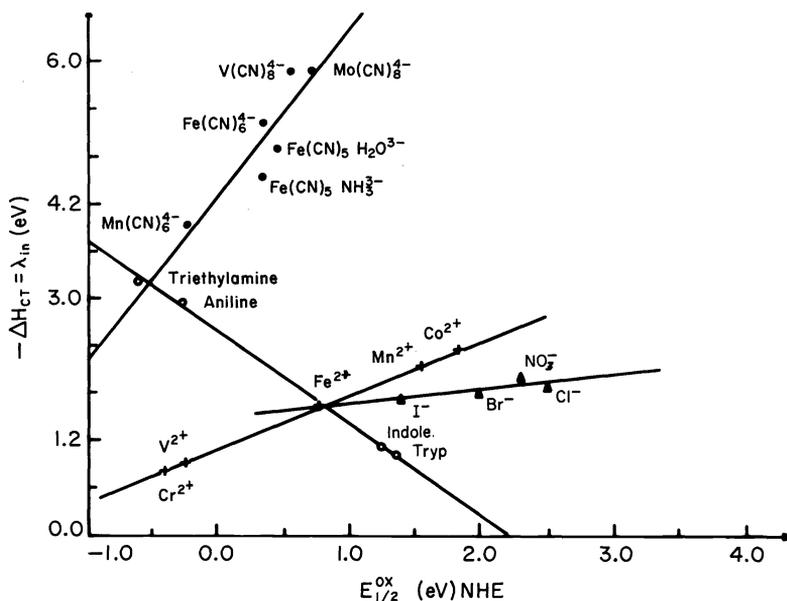
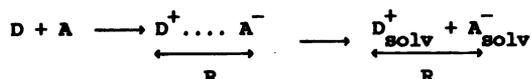


FIG. 2 Linear correlation between $\Delta H_{CT} = \lambda_{in}$ of donors and acceptors with $E_{1/2}^{ox}$ (water as solvent).

III CASE WHERE THE ACCEPTOR IS ANOTHER SOLUTE IN THE SAME SOLVENT



(solv : solvated)

a) As in the photoionization case, we consider each reactant forms with each solvent cavity a CT complex with a specific solute-solvent cage interaction energy $\Delta H_{CT} = \lambda|_n$, where i represents the species A or D. Any transfer of charge from or to the solute is through this solvent cage whose radius remains unchanged throughout the ET reactions at equilibrium conditions.

b) When the two "solvated" reactants are brought to a distance R to form an intermediate CT or ion-pair state where the electron transfer takes place (a Marcus activated state) another solvent reorganization around the solvated reactants (i. e. outside the first solvation shell of each reactant involved) is required : $\lambda_{\text{out}} = \lambda_{\text{out}}^A + \lambda_{\text{out}}^D$. In view of eq(11) and Fig. 1, we have :

$$\lambda_{\text{in}} = \lambda_{\text{in}}^A + \lambda_{\text{in}}^D = -e^2(1/D_{\text{op}} - 1/D_S)(1/2r_A + 1/2r_D) \quad (11a)$$

$$\lambda_{\text{out}} = \lambda_{\text{out}}^A + \lambda_{\text{out}}^D = e^2(1/D_{\text{op}} - 1/D_S)(1/2r_A + 1/2r_D - 1/R) \quad (11b)$$

Where r_A , r_D and R are the radius of the cavity of the acceptor A, the donor D and of the outer sphere of A and of D^+ in the ion-pair state (R is the same for both A^- and D^+) respectively.

c) The final state is the formation of the two solvated charged products D_{solv}^+ and A_{solv}^- with the corresponding solvation energy $E_S^{D^+}$ and $E_S^{A^-}$ at distance R (D_{solv}^+ and A_{solv}^- have a corresponding radius r_D and r_A).

The overall free energy change for the adiabatic ET reaction is (for detail see ref 4) :

$$\Delta G^\circ(R) = (I_D^g + E_S^{D^+}) - (E_A^g - E_S^{A^-}) + \lambda_{\text{in}} + \lambda_{\text{out}} + E_S^{D^+} + E_S^{A^-} = 0 \quad (12)$$

In solution where the solvent is homogeneous (i. e. a non-mixed solvent) the solvent optical and static dielectric constants, D_{op} and D_S , are the same in the inner shell as in the outer shell. And in view of eqs (8a) and (8b), the eq. 12 now reduces to eq 13 :

$$\Delta G^\circ(R) = (E_{1/2}^{\text{ox}} - E_{1/2}^{\text{red}} - e^2/RD_{\text{op}}) = 0 \quad (13a)$$

or

$$\Delta G^\circ = E_{1/2}^{\text{ox}} - E_{1/2}^{\text{red}} - e^2/RD_{\text{op}} \quad (13b)$$

Consequently e^2/RD_{op} is the energy necessary to separate the charged products D_{solv}^+ and A_{solv}^- at distance R to ∞ .

Eq 13b permits us to evaluate the reaction distance R between the two reactants. $1/R$ is always a linear function of ΔG° . Hence, with $\lambda = \lambda_{\text{in}} + \lambda_{\text{out}}$ according to eqs (11a) and (11b), it is the variation of λ_{in} with ΔG° which determines the variation of λ with ΔG° . As a remark, in the photoionization case the solute solvent cavity is an acceptor hence $r_A = r_D = R$. Eq. 13b becomes eq. 6 above with the reduced species as a solvated electron (Fig. 1).

Applications

The Marcus theory (3) states that the experimental rate constant k_{ET} of outsphere ET reactions is related to the activation free energy change ΔG^\ddagger by :

$$RT \ln (k_{ET}/Z) = -\Delta G^\ddagger \quad (14)$$

In which $Z = 10^{11} \text{M}^{-1} \text{S}^{-1}$ is a collision number. ΔG^\ddagger is further related to the standard free energy change ΔG° for the reaction $D + A \longrightarrow D^+ + A^-$ by :

$$\Delta G^\ddagger = \Delta G^\circ/4\lambda + (W^P - W^r + \lambda)(\Delta G^\circ/2\lambda) + \Delta G^\circ \quad (15)$$

Where ΔG° is the reaction intrinsic barrier ($\Delta G^\ddagger = \Delta G^\circ$ when $\Delta G^\circ = 0$), W^r and W^P are the free energy change when the reactants and the products respectively are brought together to the separation distance R and λ is the solvent reorganization energy of the reactivity system at distance R . λ is expressed by :

$$\lambda = \lambda_{\text{in}} + \lambda_{\text{out}} \quad (16a)$$

and

$$\lambda_{\text{out}} = e^r(1/D_{\text{op}} - 1/D_S)(1/2r_D + 1/2r_A - 1/R) \quad (16b)$$

where r_D and r_A are the radius of the solvent inner shell of D and A.

1 Case where various donors react with the same acceptor (or vice versa) with same pH and ionic-strength $E_{1/2}^{ox}$ remains constant, $E_{1/2}^{red}$ varies (or vice versa). λ_{1n}^A (or λ_{1n}^D) is then constant, λ_{1n}^D (or λ_{1n}^A) varies linearly with ΔG° (section I2C). In view of eqs (11a), (11b) and (13b), λ is thence a linear function of ΔG° . The Marcus quadratic function is now reduced to a linear function. We have $\ln k_{ET}$ varies linearly with ΔG° (Fig 3). The data in Fig.3 are taken from Rehm and Weller (2). These authors have proposed a formula to fit the data. Line A represents plots of $\ln k_{ET}$ vs ΔG° for aromatic amines (or similar compounds) as quenchers, and line B, for aromatic methoxyhydrocarbons as quenchers with various donors or acceptors. (For detail see ref 4).

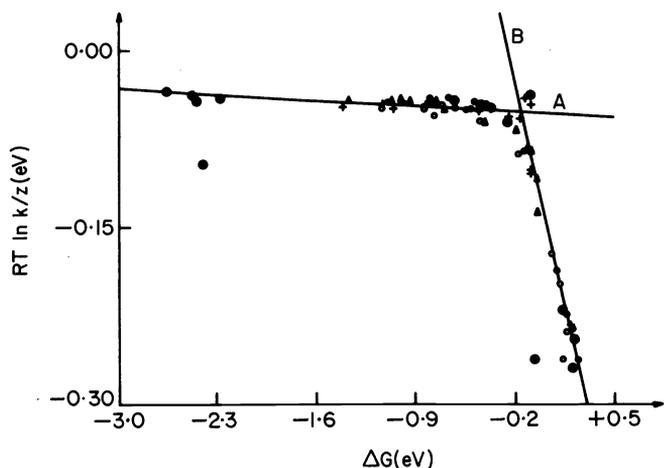


FIG.3 Linear correlation between logarithms of fluorescence quenching rate constants k and ΔG° . Line A represents various methoxybenzenes as quenchers. Data taken from ref. 2.

2 Case where both reactants remain the same, but ionic strength or added ions size varies

With increase in added co-ion size, $\ln k_{ET}$ increases linearly with ΔG° (Fig. 4). And for each change in the ionic strength we have a corresponding straight line of $\ln k_{ET}$ vs ΔG° . However with the same added co-ion size but at various ionic-strength, $\ln k_{ET}$ of the same reactant couple or of reactant couples with the similar solute-solvent configurations is no longer a linear function of ΔG° (N° 3, 4, 12, 17, 24, in Fig. 4).

The slope of the lines is positive : we have here a Marcus inverted region. The data are taken from Bruhn and al. (12) and the numbers correspond to the listed corresponding compounds in ref. 4.

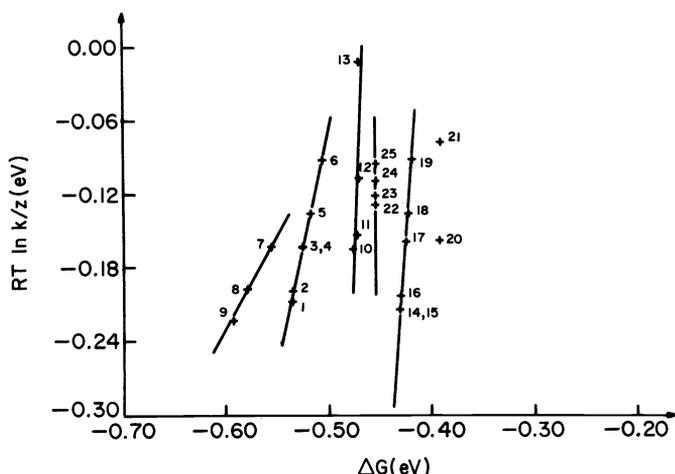


FIG.4 Effect of co-cation size on ET rate constants: linear correlation between $\ln k_{ET}$ and ΔG° . Data are taken from ref. 12.

3 Case where both reactants remain the same, but pH, ionic-strength and added co-ions size vary

The effect of pH and ionic-strength on electrolytes is to modify their redox potential : $\Delta G^\circ = E_{1/2}^{ox} - E_{1/2}^{red}$. Since λ_{1n}^D and λ_{1n}^A both vary linearly but inversely with ΔG° (Fig. 2), $\lambda_{1n} = \lambda_{1n}^A + \lambda_{1n}^D$ may no longer be a linear function of ΔG° . This leads to $\lambda = \lambda_{1n} + \lambda_{out}$ having a function which is not linear with ΔG° (section I1C) (Fig. 5 and 6). Line A in Fig. 5 represents

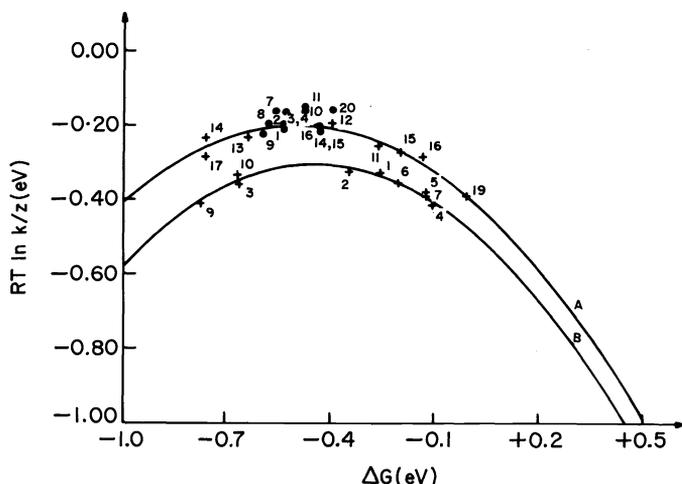


FIG. 5 Variation of $\ln k_{ET}$ vs ΔG° of ET reactions between $Fe^{2+/3+}$ complexes and various acceptors in various media. (see ref. 4 for detail).

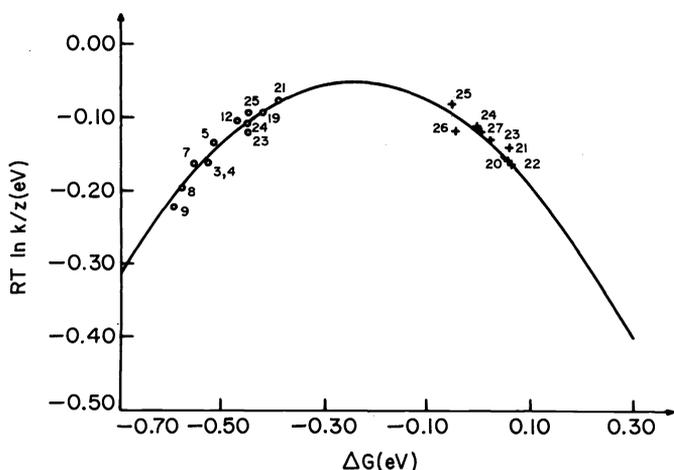


Fig. 6 k_{ET} vs ΔG° of ET reactions between $IrCl_6^{2-}$ and $Fe^{2+/3+}$ complexes or $W(CN)_6^{4-}$ or $Ag^{II}TPPTS^{4-}$ (see ref. 4 for detail).

$\ln k_{ET}$ vs ΔG° of couples with co-cations size of Li^+ , H^+ and Na^+ ; line B, with co-cations size of K^+ or similar. The pH varies from 13 to 3 and ionic strength from 0 to 3 M. In fig. 6, Bruhn et al (12) data now occupy the inverted region and only data with added co-ions size of K^+ or similar size can fit in the curve, others with smaller or larger added co-ions size are out of the curve (pH varies from 5 to 7 and ionic strength, 0.1 - 1 M).

IV CONCLUSION

The Marcus solvent reorganization energy is a function of ΔG° . But it is the variation of the Marcus λ_{1n} with ΔG° which determines the variation of the ET rate constants with ΔG° .

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