THEORY OF ELECTRON-TRANSFER REACTIONS AND OF RELATED PHENOMENA

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Abstract — Résumé — Аннотация — Resumen

THEORY OF ELECTRON-TRANSFER REACTIONS AND OF RELATED PHENOMENA. Data on electron-exchange reactions have provided insight into factors influencing rates of electron-transfer reactions in solution. The present paper has the twofold purpose of discussing some of these factors and of describing applications of these exchange data and theory to other phenomena.

The reaction rate depends upon the extent of reorganization of bond lengths (angles) in the reactants and of solvent reorientation outside them. The reorganization is facilitated or hindered in a comparatively simple way by a favorable or unfavorable standard free energy of reaction. The rate depends, too, on coulombic and other interactions, as evidenced perhaps by certain salt effects, though probably only by a few orders of magnitude typically. The observed variation of rates of some 15 orders of magnitude is best attributed primarily to differences in the vibrational reorganization term, a factor calculable from bond lengths and force constants when known. A remaining factor, non-adiabaticity, is at present of uncertain importance. Arrhenius frequency factors in chemical and electrochemical exchange rate constants would provide the most direct information, but can be complicated or even dwarfed by solvent reordering effects in the coulombic interaction. Available data are few. They provide examples where a non-adiabatic effect is minor. There appear to be no known examples where it is major (Fe^{2+} - Fe^{3+} could be a candidate but its mechanism is apparently uncertain).

Reorganization in reactants and in solvent occurs in a variety of related phenomena, and related concepts will be applied to treat them. In turn, chemical exchange data have useful applications to the latter. These areas include electrochemical exchange reactions, chemiluminescent electron-transfer reactions (between positive and negative aromatic ions, for example), and redox reactions of the solvated electron. An explanation for the chemiluminescent reactions will be based on the possible "inverse ΔF°" effect, discussed several years ago by the author. A related phenomenon involving solvent "orientation strain" occurs in light absorption or emission by polar solutes in polar solvents, and the theoretical approach used by the author for treating it is closely related to that used for the exchange reactions.

THÉORIE DES TRANSFERTS D'ÉLECTRONS ET DE PHÉNOMÈNES CONNEXES. Les données sur les échanges d'électrons ont éclairé le rôle des facteurs qui influent sur les vitesses des transferts d'électrons en solution. Le mémoire a le double objet suivant: discuter certains de ces facteurs et décrire les applications de ces données et de la théorie de l'échange à d'autres phénomènes.

La vitesse de transfert dépend du degré de la réorganisation des longueurs de liaison (angles) dans les corps réagissants et de la réorientation du solvant périphérique. La réorganisation est facilitée ou entravée d'une manière relativement simple par une énergie libre type de réaction favorable ou défavorable. La vitesse varie aussi avec les interactions coulombiennes et autres, comme le montrent peut-être certains effets salins, mais sans doute seulement de quelques ordres de grandeur. Il faut attribuer la variation observée des vitesses, de quelque quinze ordres de grandeur, surtout aux différences du terme de réorganisation vibrationnelle, facteur que l'on peut calculer à partir des longueurs de liaison et des constantes de force, lorsqu'elles sont connues. L'importance du facteur non-adiabaticité est incertaine. Les facteurs de fréquence d'Arrhénius dans les constantes de vitesse d'échange électrochimique et chimique donneraient les renseignements les plus directs, mais les effets de remise en ordre du solvant dans l'interaction coulombienne peuvent compliquer ou même minimiser leur action. Les données dont on dispose sont fragmentaires. Elles fournissent des exemples de cas où un effet non adiabatique a une importance secondaire. Il ne semble pas qu'il y ait d'exemples de cas où cet effet soit de première importance (Fe^{2+} - Fe^{3+} pourrait en être un, mais son mécanisme est apparemment incertain).

La réorganisation dans les corps réagissants et le solvant se produit dans divers phénomènes associés, et l'auteur applique des théories apparentées pour les étudier. Les données sur les échanges peuvent aussi leur être appliquées utilement. Ces questions comprennent les échanges électrochimiques, les transferts d'électrons avec chimioluminescence (par exemple, entre ions aromatiques positifs et négatifs), et les réactions d'oxydo-réduction de l'électron solvatisé. L'auteur explique les transferts avec chimioluminescence en se fondant sur la possibilité d'un effet « $\Delta F°$ inverse », qu'il a discuté quelques années auparavant. Un phénomène associé impliquant une «tension d'orientation» dans le solvant se produit dans l'absorption ou l'émission de lumière par des solutés polaires dans des solvants polaires, et la théorie appliquée par l'auteur à ce phénomène est étroitement apparentée à celle qui est appliquée aux échanges.

ТЕОРИЯ РЕАКЦИЙ ПЕРЕНОСА ЭЛЕКТРОНОВ И СВЯЗАННЫХ С ЭТИМ ЯВЛЕНИЙ. Данные по реакциям обмена электронов позволили понять факторы, влияющие на скорость реакции переноса электронов в растворе. Работа имеет двоякую цель: рассмотреть некоторые из этих факторов и описать применение этих данных и теории обмена в отношении других явлений.

Скорость реакции зависит от степени изменения длин связей (углов) в реагирующих веществах и переориентации растворителя за их пределами. Это изменение облегчается или затрудняется довольно просто благоприятными или неблагоприятными значениями стандартной свободной энергии реакции. Скорость реакции зависит также от кулоновского и других взаимодействий (о чем свидетельствуют, по-видимому, определенные солевые эффекты), хотя, вероятно, только на несколько порядков величины. Наблюдаемое изменение скоростей примерно на 15 порядков величины лучше всего объяснить изменениями составляющей, которая обусловлена колебательными изменениями и может быть рассчитана на основании длин связей и силовых констант, если они известны. Значение другого фактора (неадиабатичность) в настоящее время точно не известно. Частотные коэффициенты Аррениуса для констант скорости химического и электрохимического обмена позволили бы получить наиболее прямые данные, но они могут быть усложнены или даже занижены за счет эффектов перераспределения растворителя при кулоновском взаимодействии. В настоящее время имеются лишь немногие данные. Они служат примерами там, где неадиабатический эффект является небольшим. Примеров того, где этот эффект является большим, кажется, не существует (возможным примером могла бы быть реакция $Fe^{+2} - Fe^{+3}$, но ее механизм точно не известен).

Изменение в реагирующих веществах и в растворителе происходит при целом ряде связанных явлений, и для их объяснения будут использованы соответствующие концепции. Данные по химическому обмену будут, в свою очередь, с пользой применены для объяснения этих концепций. Эти явления включают электрохимические реакции обмена, хемилюминесцентные реакции переноса электронов (между положительными и отрицательными ионами ароматических соединений, например) и окислительно-восстановительные реакции сольватированного электрона. Объяснение хемилюминесцентных реакций будет основано на возможном эффекте "обратного ΔF^0", который рассматривался автором несколько лет назад. Связанное с этим явление, затрагивающее "деформацию ориентации" растворителя, происходит при поглощении или испускании света полярными растворенными веществами в полярных растворителях, и теоретическое объяснение, использованное автором для рассмотрения этого явления, тесно связано с тем объяснением, которое он применил для реакций обмена.

TEORIA DE LAS REACCIONES DE TRANSFERENCIA ELECTRONICA Y DE LOS FENOMENOS CONEXOS. Los datos adquiridos sobre reacciones de intercambio electrónico han contribuido a aclarar el papel de los factores que ejercen influencia sobre la velocidad de las transferencias de electrones en solución. La presente memoria tiene una doble finalidad: analizar algunos de estos factores y describir cómo se aplican a otros fenómenos esos datos y esa teoría sobre el intercambio.

La velocidad de transferencia depende del grado de reorganización de las longitudes de enlace (ángulos) en los reactivos y de la reorientación del solvente periférico. Valores favorables de la energía libre tipo de reacción facilitan esa reorganización, mientras que valores desfavorables la obstaculizan. La velocidad depende asimismo de diversas interacciones, entre ellas coulombianas, como lo ponen de manifiesto ciertos efectos salinos, si bien es probable que la influencia típica alcance sólo unos pocos órdenes de magnitud. La variación de velocidades observada, de unos 15 órdenes de magnitud, ha de atribuirse fundamentalmente a diferencias en el término de reorganización vibracional, factor que puede calcularse a partir de la longitud de los enlaces y de las constantes de fuerza, cuando ambas magnitudes se conocen. La importancia del factor de no adiabaticidad es incierta. Para las constantes de velocidad de intercambio químico y electroquímico, los factores de frecuencia de Arrhenius constituirían la información más directa; pero los efectos del reordenamiento del solvente en la interacción coulombiana pueden complicar esos factores o incluso reducir al mínimo su efecto. Los escasos datos disponibles se refieren a ejemplos donde el efecto no adiabático tiene importancia secundaria. No se

conocen, al parecer, ejemplos en los cuales ese efecto alcance una importancia primordial. (El intercambio Fe^{+2}- Fe^{+3} podría considerarse como tal, pero al parecer su mecanismo no ha podido determinarse aún con plena certeza).

En los reactivos y solventes, la reorganización se manifiesta en diversos fenómenos asociados. A su vez, los datos sobre intercambio químico pueden aplicarse con provecho a esos fenómenos. Entre éstos se incluyen intercambios electroquímicos, reacciones de transferencia de electrones con quimioluminiscencia (por ejemplo, entre iones aromáticos positivos y negativos), y reacciones de oxidorreducción donde el electrón se transfiere solvatodo. El autor explica las transferencias acompañadas de quimioluminiscencia basándose en la posibilidad de un efecto " ΔF^* inverso", que analizó hace algunos años. Un fenómeno asociado que implica una "tensión de orientación" en el solvente, aparece en la absorción o emisión de luz por parte de solutos polares en solventes también polares; el enfoque teórico empleado por el autor para estudiar este fenómeno guarda una estrecha relación con el aplicado a las reacciones de intercambio.

For this symposium I should like to summarize the assumptions of a theory of outer-sphere electron-transfer reactions [1], several experimental tests of the theory [2, 3], and several applications of these studies to other electron-transfer processes. A more detailed description of various theories and of the data has been given in a recent review article [3].

Among the principal assumptions are the following [1c, 3]: (1) the usual assumptions of using equilibrium statistical mechanics to calculate the chance that the system will form an "activated complex" and of assuming that the rate is the rate of "first passages" through activated complex configurations; (2) classical statistical mechanics for calculating the principal contributions to the free energy of activation; (3) weak overlap of the redox orbitals; (4) reaction is usually quantum-mechanically adiabatic; and (5) partial dielectric unsaturation outside co-ordination shells.

In addition, several approximations were introduced to simplify the equations considerably for easier comparison with the experimental data: (6) harmonic vibrations inside co-ordination shells; and (7) "symmetrized" potential energy surfaces of reactants and products. In some applications it is assumed (8) that specific interaction effects cancel in certain comparisons and can be ignored in others. Assumption (7) and, except when large changes of bond length occur, assumption (6) can be shown to introduce little error.[1]

Assumptions (1) to (7) lead to the following simple expression for the rate constant k of chemical or electrochemical electron-transfer reactions [1-3]:

$$k = \kappa \rho Z e^{-\Delta F^*/kT} \tag{1}$$

$$\Delta F^* = w^r + \frac{\lambda}{4}(1 + \Delta/\lambda)^2 \tag{2}$$

where $\kappa \cong 1$ (assumption (4)), $\rho \cong 1$, $Z \sim 10^{11}\ M^{-1}\ sec^{-1}$ (homogeneous) or 10^4 cm sec^{-1} (heterogeneous), Δ equals $\Delta F^{0'} - w^r + w^p$ for homogeneous reactions and equals $ne(E - E^{0'}_0) - w^r + w^p$ for electrode reactions. The remaining symbols are defined as follows: w^r, w^p = work to bring reactants together

[1] E. g. see Ref. [1c] for error estimate of (7).

or products together, respectively, to mean separation distance R in the activated complex;[2] $\Delta F^{o\prime}$ = "standard" free energy of the homogeneous reaction for the prevailing temperature and medium; n = number of electrons transferred in electrode reaction; $E - E_0'$ = cell potential minus "standard" cell potential (corrected for iR drop, etc.); λ = intrinsic reorganization factor, which depends on differences of orientation polarization and of bond lengths in the two valence states of each reacting species. λ is essentially an additive function $[=\frac{1}{2}(\lambda_a + \lambda_b)]$ of homogeneous reactants A and B. λ for the electrode reaction of species A $(=\lambda_a^{el})$ equals $\frac{1}{2}\lambda_a$ when R in the homogeneous reaction is twice the ion-electrode distance in the electrode reaction [1, 3].

From these equations a number of predictions follow involving relations between the rate constants of cross-reactions, homogeneous exchanges, and electrode reactions [2, 3]. In turn, these tests provide some insight into the applicability of the various assumptions as well as into the mechanism of the reactions. The predictions are summarized elsewhere and compared there with the data [2, 3].

A direct consequence of assumptions (5), (6) and (7) is the simplicity of the final result (e.g. Eq. (2) and the additivity of λ) as well as the fact that for small Δ's ($\Delta \ll \lambda$), $\partial\Delta F^*/\partial\Delta = 0.5$. Evidence for this numerical value of the derivative for small Δ's exists for both homogeneous and electrochemical reactions and is discussed elsewhere [2, 3].

Another consequence of assumptions (5) to (7) is the existence of a relation between the rate constant k_{ab} for $A_{ox} + B_{red} \rightarrow A_{red} + B_{ox}$ and those for the electron exchanges (k_{aa} and k_{bb}) and the equilibrium constant, K_{ab} [2]:

$$k_{ab} \cong \sqrt{k_{aa} k_{bb} K_{ab} f} \tag{3}$$

where f is a certain function of k_{aa}, k_{bb} and K_{ab}, and is usually close to unity.

Again, except for accidental cancellation, a reflection of the λ-additivity and of the 0.5 value for $\partial\Delta F^*/\partial\Delta$ is the constancy of the ratios k_a^{el}/k_{ab} and k_{ab}/k_{ac} when A is varied in a series of reactions with an electrode at a given cell potential or with a reagent B or with another reagent C (cf. reductions of $Co(NH_3)_5X^{III}$ for different X's). Evidence for such constancy is discussed elsewhere [2, 3].

Some test of (4) is available. If k is written as an Arrhenius expression $A \exp(-E_a/kT)$ then

$$A \sim \kappa \rho Z \exp(\Delta S^*/k) \tag{4}$$

where $\Delta S^* = -\partial\Delta F^*/\partial T$ and where the temperature dependence of κ on T, if any, has been neglected. A principal contribution to ΔS^* is the entropy change associated with w^r and w^p in the case of ionic reactions. The increased or decreased local electric fields in the vicinity of reactants, caused by bringing together ions of like or of unlike signs, respectively, causes increased or decreased order in the solvent molecules. In electrode reac-

[2] In an electrode reaction the electrode is one of the "reacting species". The R now refers to the ion-electrostatic image distance, i.e. to twice the ion-electrode distance [1c, 3].

tions such an effect occurs as well (ion-electrode repulsion or attraction) but is usually assumed to be swamped by high salt concentrations. In that case, $A/Z \simeq \kappa$ since $\rho \cong 1$. Evidence in support of $A/Z \sim 1$ (and so $\kappa \sim 1$) is available for electrode reactions. For homogeneous reactions, however, it may be difficult to completely swamp these electrostatic effects because of the high charges of both reactants with most reactions. Bridging effects occur and further complicate the value of ΔS^*. However, $A/Z \sim 1$ for $MnO_4^- - MnO_4^=$ under certain conditions. Studies on electron-exchange reactions of uncharged and slightly charged species would be highly desirable.

There are several occasions where some breakdown of Eq. (2) would be expected: (a) changes of bond length are so large that approximation (6) should be omitted; (b) approximation (8) breaks down.

There are several cases where relations deduced from Eq. (2) are false unless carefully calculated: (c) Eq. (3) would be false if one of these reactions involved an excited electronic state and the others did not, unless all constants referred to the same excited state; (d) separation distance in electrode reaction may be larger than that used to deduce $\lambda_a^{el} \cong \frac{1}{2}\lambda_a$.

Condition (c) might lead to enormous deviations in expected ratios of rate constants, while (a) and (b) should lead to smaller errors. (An error of only 3 kcal mole^{-1} in ΔF^*_{calc} at 25°C due to (a) or (b) causes an error of 100 in k.) In three reactions, all involving cobalt ions and summarized in the cited review [3], there were considerable deviations in the theoretical and experimental value of $k_{ab}/\sqrt{(k_{aa}k_{bb}K_{ab}f)}$, suggesting that excited states may be involved in some of these cobalt reactions. A study of reactions of the $Co(NH)_6^{2+,3+}$, $Co(phen)_3^{2+,3+}$ and $Co^{2+,3+}$ systems with a wide variety of reactants would be desirable for localizing the source of these deviations.

The λ's obtained from chemical and electrochemical rate constants have an intrinsic interest. For example, differences of equilibrium bond lengths in the two valence states of a reactant A influence the value of λ_a and reflect ligand field and other effects. The wide variation in λ_a's from system to system is expected and is presumably the principal source of the large range of k's for electron exchanges (15 orders of magnitude) and electrode exchange currents (8 orders of magnitude) [2]. The λ's also have other applications, for example to calculations for reactions of solvated electrons [4] and for chemiluminescent reactions arising from electron transfer [5].

A theoretical expression for the rate constant of electron-transfer reactions of solvated electrons has been derived elsewhere [4]. It takes cognizance of the sensitivity of the wave function of the solvated electron to fluctuations in orientation polarization of the medium, fluctuations which are required for formation of the activated complex. For very fast reactions with a substance A_{ox}, the theoretical expression for the activation controlled rate constant k_{act} reduces to Eqs. (1) and (2), with $\lambda = \lambda_a + \lambda_e$, where λ_e depends on the properties of the solvated electron, and with $\Delta F^{o\prime}$ replaced by a $\Delta F^{o\prime}_{int}$, from which it differs by an amount equal to the standard state translational free energy of the solvated electron. The "effective" standard reduction potential, used to calculate $\Delta F^{o\prime}_{int}$ from $E^{o\prime}$s of the two reactants ($\Delta F^{o\prime}_{int} = -ne(E^o_e - E^o_a)$, was estimated to be about 2.9 volts and the value of λ_e was tentatively estimated to be ca. 15 kcal mole^{-1}.

The possibility of diffusion control must be considered in these fast reactions of solvated electrons; the rate constant k_{obs} is given by:

$$\frac{1}{k_{obs}} = \frac{1}{k_{act}} + \frac{1}{k_{diff}} \tag{5}$$

where k_{diff} is the theoretical diffusion-controlled rate constant. When k_{diff} is much greater than k_{act}, k_{obs} simply equals k_{act}, and conversely. Several calculations of the rate constants of solvated electron reactions are described elsewhere [4]. They are based on λ's determined from chemical or electrochemical exchange data.

Chemiluminescent electron-transfer reactions have been the subject of several recent experimental investigations cited in Ref. [5]. They would be very exothermic if the product had been formed in its ground state instead of in an excited one, a circumstance which has some immediate consequences; some insight into the relative rates of formation of product in the two electronic states can be obtained from Eq. (2). One finds that when a reaction is so exothermic that $-\Delta F^{0\prime}/\lambda > 1$ for the ground state, the value of ΔF^* for formation of the ground state can become relatively high, while that for formation of an excited state (calculated by use of the appropriate $\Delta F^{0\prime}$ and λ for formation of that state) can be relatively small. Such conditions are favored by low λ's. (Compare the "inverse" $\Delta F^{0\prime}$ effect in Ref. [1b].)

Chemical exchange data show that the λ is low for aromatic molecules. Calculations for these reactions and for possible chemiluminescence of solvated electron reactions have been given elsewhere [4, 5]. For this purpose chemical or electrochemical λ's were employed. Arguments are also given there to show that chemiluminescent reactions would not be expected to occur on metal electrode surfaces. (Formation of an excited state of the electrode is relatively easy, and it would internally convert to its ground state.) Chemiluminescence can occur homogeneously from electrochemically generated species, however.

The dependence of orientation polarization on the charge of a species is one source of the λ term. This same dependence is also a contributing factor to the marked spectral shifts observed for certain molecules when the polarity of the solvents is changed. A detailed discussion of this phenomenon has been given elsewhere, where references to earlier work are also cited [6].

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