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Shigeru Nagase, Takayuki Fueno*

Department of Chemistry
Faculty of Engineering Science
Osaka University, Toyonaka, Osaka 560, Japan

Keiji Morokuma

Institute for Molecular Science
Myodaiji, Okazaki 444, Japan

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On the Correlation of the Kinetics of Electron-Transfer Processes with the Change in Reaction Free Energy. Application to Electron-Exchange-Initiated Chemiluminescence Reactions

Sir:

Single-electron-transfer reactions to generate radical-ion intermediates have been shown to be of crucial importance in the chemistry of organic and organometallic electronically excited states,[1] singlet oxygen,[2] radicals,[3] and organic peroxides.[4] The radical ions so produced have been observed to return to reactants (fluorescence quenching), to undergo further electron-transfer reactions that lead eventually to products, to combine to generate products, and to annihilate to form electronically excited states (chemiluminescence). Often the evidence for the involvement of radical-ion intermediates in these processes is a correlation of the observed rate constant for reaction with the one-electron oxidation or reduction potential of the reactant.[5] Our recent work on chemically initiated electron-exchange luminescence (CIEEL) has produced several such correlations.[4e-i] We report herein an interpretation of the kinetics of these apparently irreversible, endergonic, electron-transfer reactions based upon the model proposed by Weller and co-workers.[6]

Equation 1 is an adapted version of the general reaction scheme presented by Rehm and Weller:[6b]

$$\mathrm{D + A} \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} \mathrm{D\text{-}A} \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} {}^2\mathrm{D}^{+}\cdot\text{-}{}^2\mathrm{A}^{-}\cdot \xrightarrow{k_{30}} \mathrm{P} \tag{1}$$

The subscripts on the rate constants have been kept the same for consistency but the reactants have been generalized as donor (D) and acceptor (A) and the electronic states of these are left unspecified. The products (P) of the reaction may be different electronic states of the reactants or new substances. The first equilibrium defines the diffusion of the reactants, the second the electron-transfer process. It should be noted also that the final step (rate constant k_{30}) is irreversible and may correspond to diffusion apart of the ions or to chemical reaction. Application of the usual steady-state approximation to the concentration of encounter complex (D-A) and radical-ion pair (${}^2D^{+}\cdot\text{-}{}^2A^{-}\cdot$) leads to

$$k_p = \frac{k_{30}k_{23}k_{12}}{(k_{32} + k_{30})(k_{21} + k_{23}) - k_{32}k_{23}} \tag{2}$$

(analogous to eq 2 of Rehm and Weller[6b]) which defines the rate constant for formation of P (k_p). It is the correlation of this rate constant with the energetics of the electron transfer (ΔG_{23})[7] that can provide the kinetic evidence for an electron transfer in a reaction scheme. The relationship among the magnitudes of the various rate constants of eq 2 apparently determines the nature of this correlation. Weller and co-workers,[6] for example, have observed diffusion limited electron transfer for which k_p is independent of ΔG_{23} (case i, below) and endergonic electron transfer for which k_p depends strongly on ΔG_{23} (case ii, below). Our observations[4e-i] suggest a third form for the correlation of k_p with ΔG_{23} (case iii, below) which occurs when the electron-transfer step is both endergonic and irreversible.

Case i. The electron-transfer step (k_{23}) is exergonic ($\Delta G_{23} < 0$) and irreversible. The two conditions specified above are not unrelated. The reverse electron transfer (k_{32}) must be endergonic and therefore activated. Diffusion of the radical ions or chemical reaction (k_{30}) could easily be orders of magnitude larger than k_{32}[8] ($k_{32} \ll k_{30}$). Weller reports that, when ΔG_{23} is negative by more than about 5 kcal/mol, k_p is equal approximately to the diffusion-limited rate constant k_{12}; thus $k_{23} \gg k_{21}$. When these inequalities are applied to eq 2, they lead to the conclusion that, for this case, there should be no correlation between ΔG_{23} and k_p. The slope of a semilog plot of k_p against ΔG_{23} should be equal to zero, as has been seen experimentally.[6a,b]

Case ii. The electron-transfer step k_{23} is endergonic ($\Delta G_{23} > 0$) and reversible. As in the above case, these two conditions are related. Back electron transfer (k_{32}) is now the exergonic direction and since exergonic electron transfer competes effectively with diffusion $k_{32} \gg k_{30}$. By analogy, $k_{23} \ll k_{21}$. That is, diffusion is faster than activated electron transfer. When these inequalities are applied to eq 2, they lead to

$$k_p = k_{30}K_{12}K_{23} = k_{30}K_{12}e^{-\Delta G_{23}/RT} \tag{3}$$

where $K_{12} = k_{12}/k_{21}$ and $K_{23} = k_{23}/k_{32}$. With these restrictions a semilog plot of k_p against ΔG_{23} should give a line with a slope of $-1/RT$. Observation of this behavior, when ΔG_{23} is represented as a linear function of the oxidation or reduction potential of the reactant, has been taken as strong evidence for the involvement of a rate-limiting electron-transfer step on the reaction coordinate.[9] Moreover, this observation tends to support the postulate of the model that K_{12} is independent of ΔG_{23}. It should be noted that, when $\Delta G_{23} \sim 0$, the kinetics are apparently well fit by Weller's[6b] empirical equation and by Marcus' relationship.[10]

Case iii. The electron-transfer step (k_{23}) is endergonic ($\Delta G_{23} > 0$) and irreversible. As in case ii, $k_{23} \ll k_{21}$ but now $k_{32} \ll k_{30}$ as well. Such a circumstance might be realized if gain (or loss) of an electron by the reactant generated a reactive radical ion that underwent irreversible chemistry at a rate faster than the back electron transfer. Substitution of the above inequalities into eq 2 leads to

$$k_p = K_{12}k_{23} \tag{4}$$

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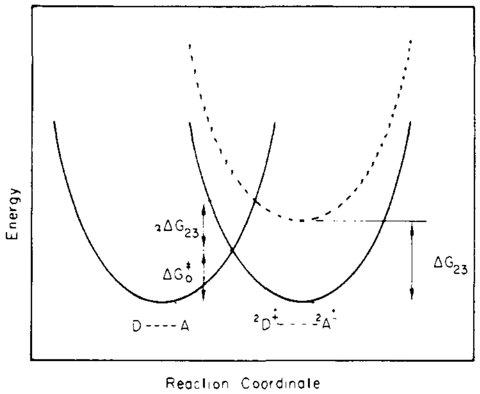

Figure 1. Relationship between ΔG_{23} and the change in free energy of activation for an endergonic electron-transfer reaction.

Shown in Figure 1 is an analysis of the Horiuchi-Polanyi relationship between $\Delta G^{\ddagger}{}_{23}$ and ΔG_{23}.[11a] When $\Delta G_{23} = 0$, the activation barrier is $\Delta G^{\ddagger}{}_{0}$ (intersection of the two solid curves) and has often been associated with solvent reorganization.[10] If we increase ΔG_{23} for the electron transfer by increasing the oxidation potential of D, for example, the activation barrier for reaction also increases (intersection of the solid and dotted curves of Figure 1) but not by the full amount of the increase in ΔG_{23}. As a consequence of the geometry of the intersection only a fraction (α) of the total free-energy change is realized as an increase in the activation barrier. The proportionality constant α is analogous to the well-known transfer coefficient which generally takes a value between 0.3 and 0.7 for electrode reactions.[11b] A similar analysis has led to an analogous interpretation of the Brønsted coefficient for acid- or base-catalyzed reactions.[11c] We can express k_{23} as a function of ΔG_{23} according to

$$k_{23} = k_{\mathrm{i}}e^{-\alpha\Delta G_{23}/RT} \tag{5}$$

where k_{i} is the rate constant for reaction when $\Delta G_{23} = 0$. Substitution of eq 5 into 4 leads to

$$k_{\mathrm{p}} = K_{12}k_{\mathrm{i}}e^{-\alpha\Delta G_{23}/RT} \tag{6}$$

which shows that, under these conditions, the slope of the semilog plot of k_{p} against ΔG_{23} is $-\alpha/RT$.[12] In the eventuality that K_{12} is somehow dependent on the value of ΔG_{23}, then the measured value of α is a composite of the transfer coefficients for the dissociation of the encounter complex and for the electron transfer.

Our investigation of the CIEEL mechanism for various peroxides[4e-i] has revealed the correlation of the rate constant of the chemiluminescent reaction with the activator oxidation potential shown in Figure 2. The simple relationship between k_{p} and ΔG_{23}, expressed in eq 6, appears to be in accord with these data. For the reactions that we have investigated $\Delta G^{\ddagger}{}_{23} \gg \Delta G^{\ddagger}{}_{0}$, and this may be a requirement for the application of eq 6. For these chemiluminescent reactions we associate k_{30} with the irreversible cleavage of the oxygen-oxygen bond of the reduced peroxide,[13] and α apparently takes a value of ~0.3.

The recent literature reveals that the kinetic behavior predicted by the requirements of case iii might be quite often observed. For example, Chan and Bruice[14] have investigated the reaction of nitroxides with 1,5-dihydroflavins and $N^{3,5}$-dimethyl-1,5-dihydrolumiflavin. Their findings indicate a one-electron-transfer process. Analysis of their data indicates that they are consistent also with the third case identified above with $\alpha = 0.32$. For this system k_{30} can be associated with proton transfer from the oxidized flavin to the reduced nitroxide. Thomas and Foote[2c] have reported on an apparent electron-transfer reaction from substituted phenols to singlet oxygen that is consistent with the third case outlined above. For this reaction k_{30} may be associated with the formation of a carbon-oxygen bond or transfer of a proton from phenol radical cation to superoxide radical anion and $\alpha = 0.44$. Bank and Juckett[15] have seen a similar correlation in a study of the reaction of sodium naphthalide with alkyl halides. In this case $\alpha = 0.23$ and k_{30} might correspond to the cleavage of the carbon-halogen bond.[16] Also, Gardner and Kochi[17] have observed a dependence of the rate of oxidation of tetraalkyllead compounds with hexachloroiridate(IV) that appears to be consistent with the model for endergonic irreversible electron transfer. For this reaction we would associate k_{30} with the cleavage of the lead-carbon bond and $\alpha = 0.39$.

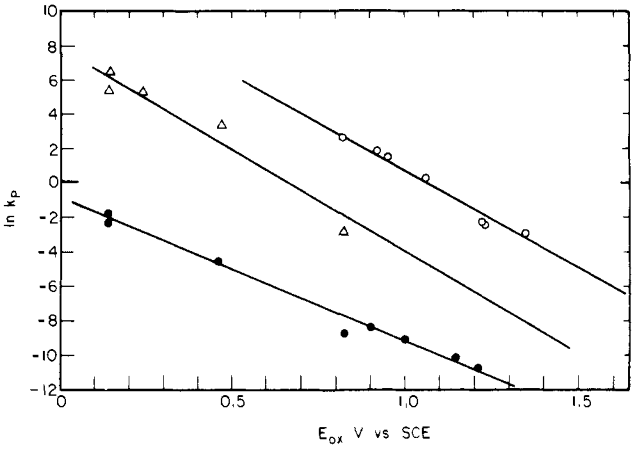

Figure 2. Dependence of k_{p} on the oxidation potential of various electron donors for the chemiluminescence of organic peroxides by the CIEEL mechanism. The open circles are for diphenoyl peroxide in CH_2Cl_2 at 27 °C, the triangles for dimethyldioxetanone in benzene at 24 °C, and the closed circles for 1-phenylethyl peroxyacetate in benzene at 99 °C. The data are taken from ref 4e-i.

In summary, we have presented an analysis of electron-transfer reactions that leads to the prediction of three limiting forms for the correlation of kinetics and energetics. Each of these forms has been observed experimentally. We are continuing our investigation of endergonic irreverisble electron-transfer reactions.

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(18) Fellow of the Alfred P. Sloan Foundation, 1977–1979.

Gary B. Schuster[18]

Department of Chemistry, Roger Adams Laboratory
University of Illinois, Urbana, Illinois 61801

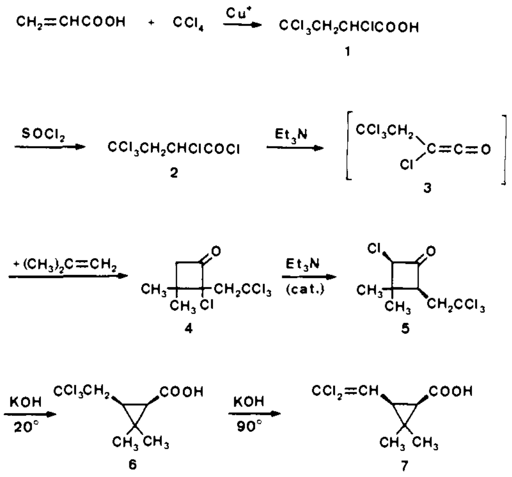
Received March 22, 1979

A Simple, Stereoselective, Highly Versatile Synthesis of Dichlorovinylcyclopropanecarboxylic Acids via 2-Chlorocyclobutanones[1]

Sir:

Recent years have seen a rapid growth in the synthetic work on pyrethroids, a class of compounds structurally related to the naturally occurring chrysanthemates.[2] Pyrethroids in general possess high insecticidal activity[3] while showing low mammalian toxicity.[4] Among modern pyrethroids, the ester of halovinylcyclopropanecarboxylic acids were found to be the most promising insecticides owing to their extraordinarily high potency and considerably increased photostability compared with those of the esters of chrysanthemic acid.[3] Consequently, there have been numerous synthetic approaches to the most important precursor, 2,2-dimethyl-3-(2′,2′-dichlorovinyl)-cyclopropane-1-carboxylic acid (**7**).[5,6]

Scheme I



All synthetic strategies to **7** published to date suffer from some serious disadvantages, e.g., a large number of synthetic steps, dangerous reagents or uneconomic processes. We now report a short, conceptually unprecedented synthesis of **7**. We believe that the underlying reactions may also have synthetic implications outside the pyrethroid field.

The copper(I)-catalyzed addition of CCl_4 to acrylic acid (0.05 molar equiv of Cu_2Cl_2, CH_3CN, 140 °C, 4.5 h) followed by treatment of the tetrachlorobutanoic acid (**1**) thus formed with thionyl chloride gave the acid chloride **2** in 76% yield (bp 79 °C (11 mm))[7] (Scheme I). The key 2-chlorocyclobutanone **4**[8] was formed by the [2 + 2] cycloaddition of isobutylene with chlorotrichloroethylketene (**3**), produced in situ from **2** (NEt_3, cyclohexane, 65 °C, 7 h, 67%). The efficient novel isomerization **4** → **5** was achieved using a catalytic amount of triethylamine (0.05 molar equiv, toluene, 120 °C, 15 h). The 4-chlorocyclobutanone **5**, isolated in 90% yield, was the thermodynamically preferred[9] 2,4-cis isomer.[10] **5** readily underwent the Favorskii rearrangement affording either **6**[11] as an 80:20 cis-trans mixture (2 molar equiv of NaOH, H_2O, 25 °C, 4 h, 89%)[12] or under subsequent HCl elimination (NaOH, H_2O, 100 °C, 6 h)—with or without the isolation of **6**—the desired acid **7**[14] in 82% yield with the same stereochemical preference (80:20) for the biologically more interesting cis isomer. Once formed, **6** and **7** proved to be entirely stable to stereoisomerization under alkaline reaction conditions.

From the synthetic point of view several noteworthy features follow: (a) the new *chlorotrichloroethylketene* **3** gives even higher yields of [2 + 2] cycloadducts than one of the most reactive ketene known so far, dichloroketene,[15] and it is the synthetic equivalent of the considerably less reactive chloro-2,2-dichlorovinylketene;[19] (b) a large variety of cyclobutanones of type **4** can readily be prepared using 1,1-dialkyl-substituted ethylenes $R_1R_2C{=}CH_2$ in place of isobutylene; and (c) the "*cine rearrangement*"[20] (e.g., **4** → **5**) proved to be a very useful synthetic reaction providing an excellent new entry into cyclopropanecarboxylic acids of type **7** (2-R_1,2-R_2 = alkyl instead of 2,2-dimethyl) via their precursors of type **5**, which would not be readily accessible by alternative methods.[21]

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