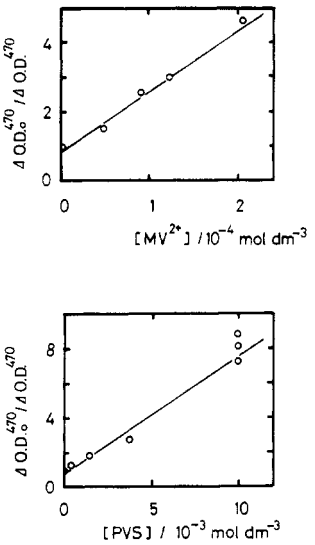

Figure 11. Relation between $\Delta OD_0^{470}/\Delta OD^{470}$ and [viologen].

The concentration of PQ increases with the increase of Q concentration. The absorbance of the T–T absorption at 470 nm is considered to be proportional to the concentration of uncomplexed $Zn(TPPS)_3^{3-}$ on the assumption that the photoexcited complex (PQ*) goes back to PQ very rapidly without the formation of the separated ion pairs. The concentration of the uncomplexed $Zn(TPPS)_3^{3-}$ can be written as eq. 4 when the 1:1 complex is

$$[P] = [P]_0/(1 + K[Q]) \quad (4)$$

formed, with $[P]_0$ and [Q] being the concentrations of $Zn(TPPS)_3^{3-}$ and viologen added, respectively. Therefore, the following relation can be derived

$$\Delta OD_0^{470}/\Delta OD^{470} = 1 + K[Q] \quad (5)$$

where ΔOD_0^{470} and ΔOD^{470} are the difference absorbance at 470 nm measured immediately after the laser flash in the absence and in the presence of viologen, respectively.

As shown in Figure 11, the fairly linear relationship between $\Delta OD_0^{470}/\Delta OD^{470}$ and [Q] indicated that the scheme proposed with some assumption described above is adequate. From the slope of the straight line in Figure 11, the value of K obtained was (1.7 ± 0.2) × 10^4 mol^{-1} dm^3 in the case of MV^{2+} and (7.3 ± 0.6) × 10^2 mol^{-1} dm^3 for PVS. The difference of K values between MV^{2+} and PVS is also explained by the difference of the electrostatic interaction between $Zn(TPPS)_3^{3-}$ and viologens.

TABLE II: Efficiency of Charge Separation and the Association Constants between $Zn(TPPS)_3^{3-}$ and Viologens

quencher	Φ_{rel}	K/mol^{-1} dm^3
MV^{2+}	1.0	(1.7 ± 0.2) × 10^4
PVS	1.6	(7.3 ± 0.6) × 10^2

The difference between the redox potential of $MV^{2+/+}$ and that of $PVS^{0/-}$ is so small that the large K value of MV^{2+} compared with that of PVS should be mainly due to an electrostatic effect. Since the positively charged MV^{2+} is more favorably associated with negatively charged $Zn(TPPS)_3^{3-}$, the large K value detected for MV^{2+} compared with PVS is plausible.

As the complexes formed between $Zn(TPPS)_3^{3-}$ and viologens (PQ) did not produce separated ion pairs as described above, PQ was not favorable for the photoreduction of viologens. Therefore it may be concluded that only the uncomplexed $Zn(TPPS)_3^{3-}$ acts as a photosensitizer for the photoreduction of viologens.

The parameters obtained in this study are summarized in in Table II. The fact that the reduction rate of PVS under steady-state irradiation was larger than that of MV^{2+} was explained by the difference of Φ_{rel} and K values; i.e., the Φ_{rel} value of PVS was larger than that of MV^{2+}, and the K value of PVS was smaller than that of MV^{2+}. As the larger K value means the high concentration of PQ which is inactive for the photoreduction of viologens, the concentration of uncomplexed $Zn(TPPS)_3^{3-}$ is greater in the $Zn(TPPS)_3^{3-}$–PVS system than that in the $Zn(TPPS)_3^{3-}$–MV^{2+} system at the same concentration of viologens. Therefore the reduction rate of PVS was larger than that of MV^{2+} under the steady-state irradiation.

Acknowledgment. We thank Dr. M. Hoshino of The Institute of Physical and Chemical Research for the measurement of the laser flash photolysis.

Registry No. MV^{2+}, 4685-14-7; $Zn(TPPS)_3^{3-}$, 95646-69-8; $HS(CH_2)_2OH$, 60-24-2; 1,1′-dipropylviologen sulfonate, 77951-49-6.

Potassium Coadsorption Induced Dissociation of CO on the Rh(111) Crystal Surface: An Isotope Mixing Study

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The formation of $^{13}C^{18}O$ from a mixture of $^{13}C^{16}O$ and $^{12}C^{18}O$ proves unequivocally that molecular CO dissociates on Rh(111) when potassium is coadsorbed. The presence of a surface complex between the alkali metal and the CO is confirmed by the simultaneous desorption of potassium and CO. A minimum of 0.08 potassium atoms per surface Rh atom is necessary to induce any CO dissociation. A maximum of three CO molecules are observed to dissociate per potassium atom.

Introduction

The influence of alkali metals on the chemisorptive properties of CO is dramatic. It is, in fact, one of the most important and interesting examples of the ability of additives to modify the chemical properties of surfaces. Previous investigations on the Rh(111)[1] and Pt(111) surfaces[2] using electron energy loss spectroscopy (EELS) have demonstrated that alkalis cause considerable carbon–oxygen bond weakening and simultaneous strengthening of the M–CO surface bond. This was concluded from observed changes in the corresponding bond vibrational frequencies, namely, substantial decreases in the C–O stretching frequencies and slight increases in the M–C vibrational frequencies.

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Furthermore, on both surfaces, temperature programmed desorption (TPD) spectra of CO shift to higher temperatures indicating increased desorption energy in the presence of potassium. This shift of desorption peak to higher temperatures is continuous on Pt(111) with increasing K concentration,[2] but distinct higher temperature states are apparent when CO is adsorbed with K on Rh(111). The origin of these potassium induced desorption states is unclear; they may be due to first-order molecular desorption of CO with the change in desorption temperature corresponding to the observed increase in the M–C stretch in EELS. Alternatively, these states may be due to second-order atom-recombination reactions of carbon and oxygen on the surface produced by alkali induced CO dissociation. It should be emphasized that the vibrational spectroscopy data do not indicate whether CO bond cleavage occurs since no significant M–O or M–C vibrations were detectable. However, an unequivocal method of deciding if a molecular desorption peak arises from dissociated adspecies is to use isotope mixing measurements. In these experiments, an alkali predosed surface is exposed to a known mixture of $^{13}C^{16}O$ and $^{12}C^{18}O$ and the desorption products are monitored at 28, 29, 30, and 31 amu. The appearance of a 31-amu signal indicates that isotopic scrambling has occurred which must indicate high-temperature CO dissociation on the surface.

The purpose of this paper is to examine whether CO is dissociated in ultrahigh vacuum in the presence of K on Rh(111). Previous studies by Yates and co-workers[3] have shown that, below 800 K, CO does not dissociate at low pressure ($\sim 2 \times 10^{-6}$ torr of CO) on clean Rh(111). Isotope scrambling in the presence of K would demonstrate that alkalis not only weaken the C–O bond but can ultimately lead to its rupture. Our isotope studies clearly indicate that coadsorbed potassium induces the dissociation of CO. At an optimum potassium coverage $\Theta_K = 0.1$, as much as three CO molecules may dissociate per potassium.

Experimental Section

The experiments were performed in an ultrahigh-vacuum system equipped with a retarding field analyzer for LEED analysis, a glancing incidence electron gun for Auger excitation, sputtering capabilities, and a quadrupole mass spectrometer for TPD studies. The chamber is maintained at base pressures, typically less than 1×10^{-10} torr, with an ion and titanium sublimation pump. The sample, a Rh(111) single crystal oriented and polished on both sides, was mounted on 0.25-mm Ta support wires. The sample was resistively heated and the temperature measured by a chromel–alumel thermocouple spot-welded to the back face of the crystal. The sample was cleaned on both sides by a combination of chemical treatment with oxygen, Ar^+ sputtering, and annealing in vacuum. LEED and AES were used to ensure that the crystal was clean and well-ordered.

Potassium atoms were deposited onto the Rh(111) surface by heating a commercial getter source (SAES) positioned ~ 5 cm from the sample. Potassium coverages were calibrated by using LEED, AES, and TPD yield as described elsewhere.[4] A monolayer of potassium corresponds to a surface density of 5.8×10^{14} atoms/cm^2, a surface coverage (Θ_K) of 0.36 potassium atoms per surface rhodium atom.

The sample was typically dosed at 140 K with potassium, followed by CO exposure using a variable leak valve and directional doser. The CO gas exposures (either $^{12}C^{16}O$ or a mixture of $^{13}C^{16}O$ and $^{12}C^{18}O$) are uncorrected for ion gauge sensitivity. The TPD results were obtained by heating the sample linearly as a function of time and monitoring the desorbing species. The change in pressure of several masses were simultaneously recorded vs. either time or temperature by using a microcomputer.

Results

Representative TPD spectra for saturation CO exposures ($^{12}C^{16}O$) on Rh(111) at 300 K as a function of predosed potassium coverage are shown in Figure 1. In these experiments, back face adsorption of CO was masked by predosing multilayers of potassium onto the back face prior to CO exposure; CO does not adsorb on pure potassium multilayers at low pressure. Initially, the effect of K is to broaden the desorption peak for the clean sample to higher temperatures. However, when a critical potassium coverage is reached ($\Theta_K = 0.1$), two new desorption states become populated. These states occur at 630 and 700 K at a heating rate of 15 K/s. These states grow in intensity with increasing potassium coverage as the low-temperature molecular states decreases in intensity. Desorption occurs only from the high-temperature 700 K state at coverages near saturation (e.g., $\Theta_K = 0.33$ in Figure 1). At coverages greater than $\Theta_K = 0.36$, no CO desorption is observed at 10-langmuir exposure.

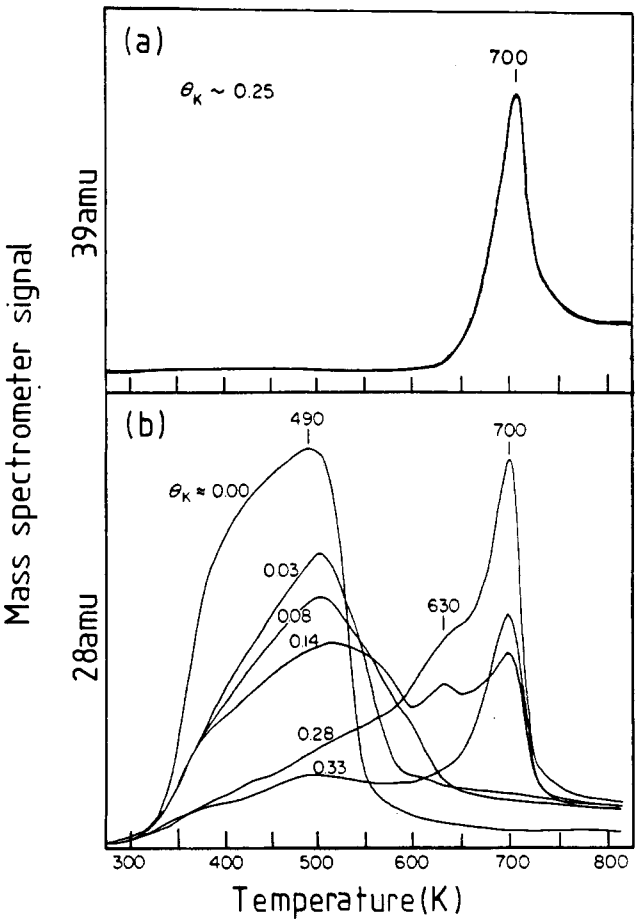

Figure 1. Thermal desorption spectra from coadsorbed K and CO on Rh(111) (a) at 39 amu for Co saturation and $\theta_K = 0.25$ and (b) at 28 amu as a function of K dose at saturation CO exposure.

The origin of these high-temperature states is discernible by adsorbing isotopic mixtures of CO. Figure 2 shows the TD spectra for surfaces predosed at 140 K with potassium and exposed to 10-langmuir of a mixture of $^{13}C^{16}O$ and $^{12}C^{18}O$. Shown are the signals at 29, 30, and 31 amu which were monitored simultaneously. Notice that $^{13}C^{18}O$ desorbs at each of the three desorption states. Adsorption of isotopic CO on the clean Rh(111) surface indicates that 6.5% of the adsorbed CO desorbs as $^{13}C^{18}O$. Similar results by Yates et al.[3] suggest that a portion of the desorbing CO are dissociated by the mass spectrometer ionizing filament. Hence, the small peak at 500 K in the 31-amu TPD spectrum is not indicative of any surface scrambling for this state.

From Figure 2, it is immediately obvious that the percentage of desorption of CO at 31 amu is larger for the two high-temperature states. This indicates that these states arise from a process which involves C and O scrambling and hence from dissociated CO.

It should be pointed out that the spectra in Figure 2 include contributions from the crystal back face (which was not alkali dosed and hence does not dissociate CO). However, this con-

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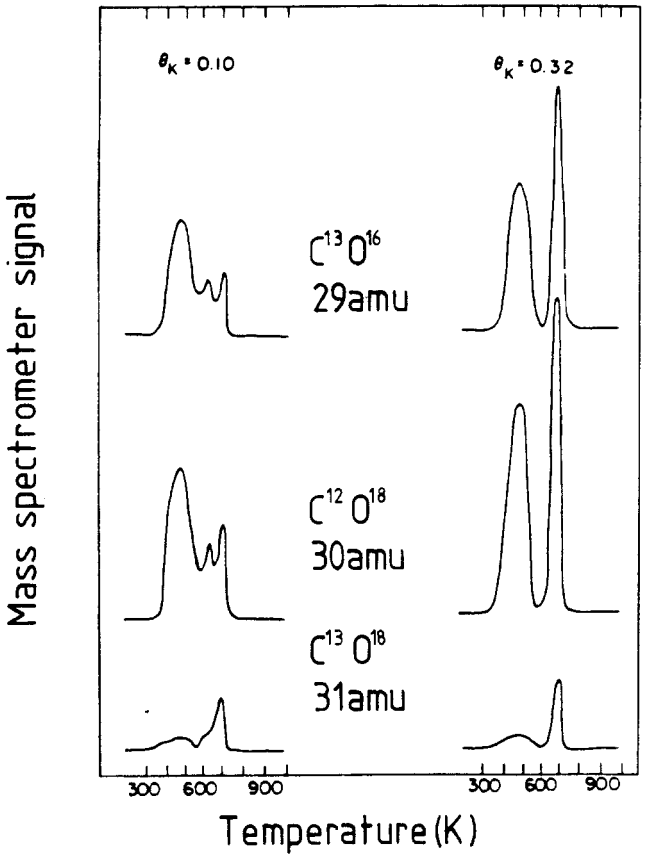

Figure 2. Thermal desorption spectra after dosing a mixture of $^{13}C^{16}O$ and $^{12}C^{18}O$ onto a potassium predosed surface for $\Theta_K = 0.1$ and 0.32.

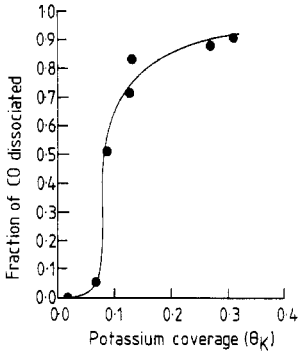

Figure 3. Plot of fraction of CO dissociated on Rh(111) as a function of potassium dose.

tribution could be measured by masking the crystal front face by saturating it with potassium. Data shown subsequently have been corrected for back face contributions.

The proportion of CO dissociating on the surface is shown vs. potassium coverage in Figure 3. The proportion of dissociation is near zero until $\Theta_K = 0.10$, where a sharp rise occurs and nearly all the CO has dissociated for a potassium coverages of $\Theta_K > 0.10$. A criterion for whether dissociation has taken place can be related to the isotopically labeled TPD spectra by defining a scrambling parameter

$$p = \frac{A_{31}}{A_{29}A_{30}}$$

where A_n is the area under the 700 K peak at n amu. A value of p of zero indicates that the carbon and oxygen are completely correlated; i.e., no dissociation has taken place. Conversely, $p = 1$ indicates total randomization of the carbon and oxygen. However, since some $^{13}C^{18}O$ is produced by the hot electron emitting filament in the mass spectrometer ionizer the minimum value of p (no surface scrambling) is 0.14. Isotopic scrambling takes place when p exceeds this value. In the limit of complete

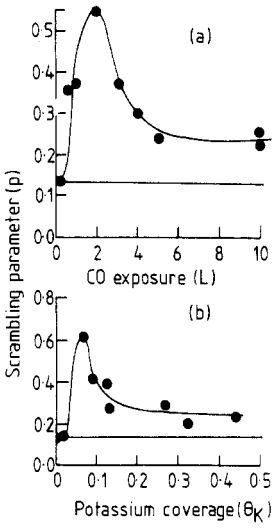

Figure 4. Plot of the variation of the scrambling parameter, p, as a function of (a) CO exposure (langmuir for a potassium coverage $\theta_K = 0.3$ and (b) potassium coverage.

scrambling (in which the dissociated atoms are completely mobile on the surface), p tends to unity. Intermediate values imply that, although dissociation takes place, the mobility of the atoms is small such that they have a higher probability of recombining with the atom to which they were originally attached. For constant CO exposure (i.e., saturation exposure) as a function of K coverage (Figure 4b), p increases from zero at $\Theta_K = 0$ to a maximum of 0.6 at $\Theta_K = 0.1$ and then slowly decreases with increasing Θ_K. Similarly, at a constant K coverage of 0.3 as a function of CO exposure, as shown in Figure 4a, a maximum in p occurs at an exposure of 2 langmuir. Significant changes in the potassium TPD spectra accompany changes in the these high-temperature states due to dissociated CO. Potassium TPD on clean Rh(111) is characterized by a desorption maximum near 1100 K at low coverages ($\Theta = 0.02$). The maximum desorption rate shifts rapidly to lower temperatures with increasing coverages and peaks at 500 K at completion of the first layer ($\Theta_K = 0.36$). The second layer desorption maximum then begins to grow in at 350 K.[4] When CO is coadsorbed with low coverages of potassium (i.e., $\Theta_K \leq 0.10$), this desorption behavior is unchanged as all the CO desorbs prior to any potassium desorption. However, once a critical potassium coverage is reached such that the two high-temperature CO desorption states are present indicating that CO dissociation has occurred, no potassium desorbs until 700 K (at a heating rate of 15 K/s). Figure 1 shows a typical desorption spectrum observed in this potassium coverage range when CO is coadsorbed. The desorption maximum is identical with that of the highest CO desorption state (700 K), suggesting an interaction between K and the dissociated CO species. For K exposures near saturation of the first layer, much less CO can be adsorbed and potassium desorption maximum at both 500 K (i.e., clean surface behavior) and 700 K (i.e., co-adsorbed CO behavior) are observed in the K TPD spectrum. Similar behavior has been seen with coadsorbed oxygen, both on Rh(111),[4] Pt(111)[5] and Ni(111).[6] Attempts to observe the desorption of potassium oxides (i.e., KO, K_2O, KO_2) were made, but no signals from these species were detected. Very small amounts of CO_2 were detected at 700 K.

Discussion

Preadsorbed K broadens the coadsorbed CO desorption spectrum by 100 K for $\Theta_K < 0.10$ and induces new desorption states in the potassium coverage range $0.10 < \Theta_K < 0.36$. Isotopic mixing measurements have demonstrated that these high-temperature states are due to recombination of carbon and oxygen produced

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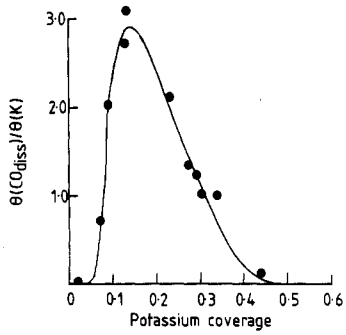

Figure 5. Plot of the number of CO molecules dissociated per potassium atom as a function of potassium coverage.

by the dissociation of adsorbed CO. The extent to which scrambling of the isotopically labeled CO molecule occurs depends on both K coverage and CO exposure.

The plot of the fraction of CO dissociated as a function of K coverage (Figure 3) demonstrates that the effect of the alkali on the number of molecules dissociating is very pronounced. Over 80% of the adsorbed CO dissociates at $\Theta_K = 0.15$. Using the CO saturation coverage of $\Theta_{CO} = 0.75$ for the clean Rh(111) surface made it possible to determine the number of CO molecules which dissociate per adsorbed K atom. Such a curve is plotted in Figure 5 as a function of K coverage. Up to three CO molecules dissociate per coadsorbed potassium atom at a coverage $\Theta_K = 0.1$, a very marked effect indeed. The curve rapidly attains a maximum, followed by a gradual decrease. This suggests that (1) a critical potassium coverage (i.e., potassium separation) is needed to induce CO dissociation, and (2) site blocking by potassium at higher coverages limits CO adsorption. This results in the ratio CO_{diss}/K decreasing slowly as the potassium coverage increases. These competitive effects result in a peak maximum. Recent calculations by Norskov et al.[7] suggest that sites adjacent to the alkali should be very strongly affected by the alkali, whereas the second nearest neighbors experience a much reduced effect. These results are consistent with our data since the number of CO molecules that dissociate is that which would be expected to pack adjacent to an isolated K atom.

Results on CO coadsorption with Na on Ru[8] suggest that the alkali is well dispersed on the surface at all coverages, thus permitting access of several carbon monoxide molecules to each alkali atom.

The simultaneous desorption of CO and K in the high-temperature state as shown in Figure 1 indicates that potassium and either C or O (or both) are associated with one another and that the rate-limiting step is the decomposition of this surface complex.

Measurement of the scrambling parameter yields a value of p considerably larger than that expected for molecular desorption, confirming that the highest temperature states are indeed due to dissociated CO. The behavior as a function of CO exposure can be explained by assuming that isolated C or O atoms (or both species) have some mobility on the Rh(111) surface. At low CO coverages (Figure 4a) the C and O adatoms from different molecules are sufficiently remote from each other that the probability of scrambling is small. As the coverage increases, the fragments from different molecules come into closer proximity and can then scramble. At even higher coverages the atoms become less mobile, either since they are close packed or because they are associated with potassium and are thus immobilized, inhibiting significant scrambling.

Finally, it should be emphasized that EEL spectroscopy shows no evidence that potassium causes CO to dissociate on the Rh(111) surface[1] since no C–metal or O–metal vibrations are observed. TPD evidence clearly indicates that CO does indeed dissociate on a potassium predosed surface, and the absence of any EELS evidence of dissociated CO on the surface may be suggestive that the dissociation (and scrambling) and desorption occur as a concerted process.

Conclusion

The coadsorption of potassium with CO on Rh(111) induces dramatic changes in the chemisorption properties of CO. Isotopic mixing measurements verify that CO dissociation occurs with coadsorbed potassium ($\Theta_K > 0.10$) but does not occur on the potassium-free Rh(111) surface. The simultaneous desorption of potassium and CO for the dissociated state indicates that direct interactions are responsible for CO dissociation and that up to three CO molecules are dissociated per potassium atom.

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Registry No. K, 7440-09-7; CO, 630-08-0; Rh, 7440-16-6.

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Noncontinuum Solvent Effects upon the Intrinsic Free-Energy Barrier for Electron-Transfer Reactions

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A phenomenological electrochemical approach is outlined by which "noncontinuum" contributions to the outer-shell intrinsic barrier to electron transfer, ΔG^*_{os}, resulting from specific reactant–solvent interactions can be estimated from the measured dependence of the formal potential upon the molecular and structural properties of the solvent. A simplified derivation, based on electrochemical half-reactions, of the conventional dielectric continuum expression is given in order to clarify the physical origins of the outer-shell intrinsic barrier and to identify likely additional noncontinuum components. Numerical calculations for ammine and other redox couples involving specific ligand–solvent interactions indicate that the noncontinuum contributions to ΔG^*_{os} for both homogeneous and electrochemical exchange reactions can be surprisingly small (typically $\lesssim$1–2 kcal mol^{-1}) even when the thermodynamics of ion solvation are in severe disagreement with the dielectric continuum (Born) predictions. An additional noncontinuum component associated with vibrational distortions of outer-shell solvent may be significant for multicharged aquo complexes and other reactants engaging in strong ligand–solvent hydrogen bonding.

In recent years a number of theoretical approaches have been developed in order to describe the kinetics of outer-sphere electron-transfer processes.[1] It is useful to divide the overall free energy of activation into so-called "intrinsic" and "thermodynamic"

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