Correspondence

Dynamics of Excited-State Rearrangement Processes in the Photochemistry of Transition-Metal Complexes

Sir:

Models[1] have been proposed for the stereochemical rearrangements often observed during the ligand field photosubstitution reactions of d^3 and d^6 transition-metal complexes. For the d^6 systems, we have expanded on this theoretical treatment[2] and supported this theory through a number of experimental papers.[2-6] The model[1,2] can be briefly outlined as follows for the d^6 system. (1) Photosubstitution of $[MA_4XY]$ occurs by loss of Y in the lowest triplet state. (2) With use of cis and trans to denote the positions of X and the vacant site, it is found that *cis*- and *trans*-$[MA_4X]$ are separated by an often low-activation barrier at the trigonal-bipyramidal structure when the triplet electronic configuration is maintained during loss of Y. (3) For the triplet $[MA_4X]$ fragment, the trans structure is favored when $e_\sigma{}^A > e_\sigma{}^X$ [1,2] while the cis structure is favored when $e_\sigma{}^X > e_\sigma{}^A$.[2] Thus, specific product geometries are expected and usually observed[2-8] when rearrangement is faster than triplet → singlet deactivation of the $[MA_4X]$ fragment.

A recent report[9] in this journal has argued that this model does not apply to d^5 systems (specifically *cis*- and *trans*-$Ru(en)_2Cl_2{}^+$) and raises doubt on its applicability to the $M(en)_2XY^{n+}$ d^6 systems studied by our group (M = Rh(III))[3-6] and Ford's group (M = Ir(III)).[10] To the contrary, Ford's interpretation of the Ir(III) work[10] and our interpretation of the d^6 [2-6] and d^5 work are compatible with the excited-state rearrangement model and demonstrate the dynamics of the rearrangement/deactivation processes involved.

Figure 1 represents the simplest way to look at the application of the excited-state model to the rearrangement process in $M(en)_2X$ systems.[10] It should be noted that a true equilibrium situation does not exist between $SP_{apical}{}^*$ and $SP_{basal}{}^*$ because of the complications of the nonradiative deactivation steps k_{na} and k_{nb}. Some limiting cases come out of this treatment and are outlined with experimental examples as follows. (1) $k_{ba} \gg k_{ab}$, k_{nb} or $k_{na} > k_{ba} \gg k_{nb}$ results in only trans products (e.g., M = Rh(III), X = Cl[3], Br,[4] I[5]). (2) $k_{ab} \gg k_{ba}$, k_{na} or $k_{nb} > k_{ab} \gg k_{na}$ results in only cis products (e.g., M = Co(III), X = CN^2; M = Ir(III), X = OH^{10}). (3) k_{na}, $k_{nb} \gg k_{ab}$, k_{ba} results in only stereoretentive products (e.g., M = Rh(III), X = NH_3 at 25 °C.[3-7] [For this system, photolysis at 50 °C leads to a cis/trans mixture of products regardless of whether $SP_{apical}{}^*$ or $SP_{basal}{}^*$ is formed initially.[7] This observation comes as a result of k_{ab} and k_{ba} becoming competitive with k_{na} and k_{nb} at higher temperatures, owing to the Arrhenius nature of the former rate constants and the relative temperature independence of the latter rate constants.[11]]

When k_{ab}, k_{ba}, k_{na}, and k_{nb} are all competitive, a mixture of products is obtained and, more importantly, *the cis/trans product ratio will be different for initial formation of* $SP_{apical}{}^*$ *(photolysis of trans reactant) and initial formation of* $SP_{basal}{}^*$ *(photolysis of cis reactant)*. For $[Ir(en)_2X^{2+}]^*$, the constraints on the rate constants correspond to X = Cl, $k_{na} \gg k_{ab}$, $k_{nb} \simeq 9k_{ba}$, for X = Br $k_{na} \gg k_{ab}$, $k_{nb} \simeq 2.3\ k_{ba}$, for X = I, and $k_{na} \gg k_{ab}$, $k_{ba} \gg k_{nb}$, for X = I as suggested by Ford.[10]

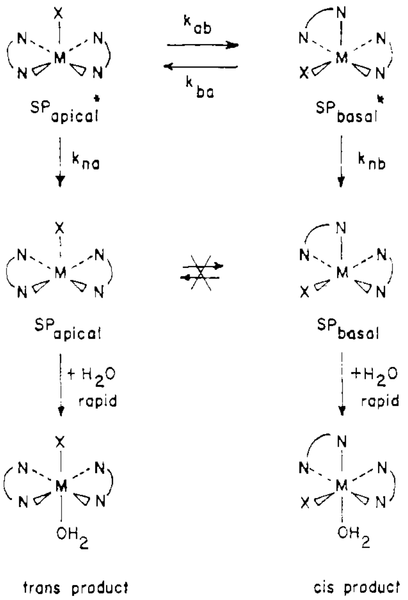
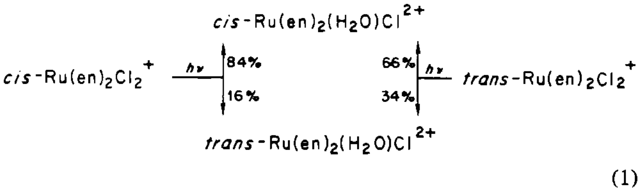


Figure 1. Dynamics of the five-coordinate fragment rearrangement and deactivation. $SP_{apical}{}^*$ and $SP_{basal}{}^*$ refer to the lowest excited-state electronic configuration (quartet for d^5, triplet for d^6) and SP_{apical} and SP_{basal} represent the ground-state electronic configuration (doublet for d^5, singlet for d^6) for the five-coordinate fragments. The individual rate constants pertain to the following processes: k_{ab}, rearrangement of $SP_{apical}{}^* \rightarrow SP_{basal}{}^*$; k_{ba}, rearrangement of $SP_{basal}{}^* \rightarrow SP_{apical}{}^*$; k_{na} and k_{nb}, deactivation of $SP^* \rightarrow SP$ for the apical and basal conformations, respectively.

The situation in the d^5 Ru(III) system, *cis*- and *trans*-$Ru(en)_2Cl_2{}^+$, is very interesting in that irradiation of either isomer results is a different cis/trans mixture of the $Ru(en)_2(H_2O)Cl^{2+}$ photoproduct (eq 1).[9] The situation outlined in



(1)

eq 1 still fits the excited-state model with an infinite number of solutions. For example, if we assume for $[Ru(en)_2Cl^{2+}]^*$ that $k_{na} = k_{nb}$, the relative rate constants that satisfy the product distribution in eq 1 are $k_{ab} = 4.0k_{ba}$ and $k_{na} = k_{nb} = 1.1k_{ba}$. However, the above relative rate constants place the energy of $SP_{basal}{}^*$ below that of $SP_{apical}{}^*$.

In our initial theoretical work on d^6 systems,[2] we calculated excited-state treatment (including configuration interaction and spin-orbit coupling) and found the two methods gave the same qualitative result. With use of a one-electron model for the d^5 system, the lowest quartet state should favor $SP_{axial}{}^*$ over $SP_{basal}{}^*$ by $^3/_4[e_\sigma(en) - e_\sigma(Cl)]$ rather than the reverse

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[1] Vanquickenborne, L. G.; Ceulemans, A. *J. Am. Chem. Soc.* **1978**, *100*, 475; *Inorg. Chem.* **1978**, *17*, 2730.
[2] Purcell, K. F.; Clark, S. F.; Petersen, J. D. *Inorg. Chem.* **1980**, *19*, 2183.
[3] Petersen, J. D.; Jakse, F. P. *Inorg. Chem.* **1979**, *18*, 1818.
[4] Clark, S. F.; Petersen, J. D. *Inorg. Chem.* **1979**, *18*, 3394.
[5] Clark, S. F.; Petersen, J. D. *Inorg. Chem.* **1980**, *19*, 2917.
[6] Clark, S. F.; Petersen, J. D. *Inorg. Chem.*, in press.
[7] Strauss, D.; Ford, P. C. *J. Chem. Soc., Chem. Commun.* **1977**, 194.
[8] Skibsted, L. H.; Ford, P. C. *J. Chem. Soc., Chem. Commun.* **1979**, 853.
[9] Rerek, M. E.; Sheridan, P. S. *Inorg. Chem.* **1980**, *19*, 2646.
[10] Talebinasab-Sarvari, M.; Ford, P. C. *Inorg. Chem.* **1980**, *19*, 2640.
[11] Petersen, J. D.; Ford, P. C. *J. Phys. Chem.* **1974**, *78*, 1144.

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suggested by the prominence of cis products in eq 1. If the one-electron model is an accurate representation of the relative energies of the excited-state fragments, the results in eq 1 can still be explained by the stereochemical rearrangement model. If we arbitrarily set the rate constants pertaining to rearrangement as $k_{ba} = 8k_{ab}$, then the relative rate constants $k_{ab} = 3.5k_{na}$, $k_{ba} = 28k_{na}$, and $k_{nb} = 34k_{na}$ mimic the experimental values in eq 1. However, these results require that deactivation of SP_{basal}* be much more rapid than deactivation of SP_{axial}*.

The fact that the series of M(III) systems d^5 Ru(III),[9] d^6 Rh(III),[3-7] and d^6 Ir(III)[10] show varying degrees of excited-state rearrangement when the $[M(en)_2Cl^{2+}]$* fragment is formed is not surprising. The ability to traverse the barrier in both directions (SP_{apical}* $\leftrightarrow$ SP_{basal}*) for Ru(III), in only one direction for Rh(III) (SP_{basal}* $\rightarrow$ SP_{apical}*), and only a small amount in one direction (SP_{basal}* $\rightarrow$ some SP_{apical}*) for Ir(III) can be linked to both the absolute magnitude of $e_\sigma{}^i$ values (Ir(III) > Rh(III) > Ru(III)) and the spin–orbit coupling constant (Ir(III) > Rh(III) $\simeq$ Ru(II)) which should make k_{na} and k_{nb} larger for the third-row Ir(III).

The current experimental data on d^6 system[12] of Rh(III)[3-7] and Ir(III)[10] are consistent with the stereochemical rearrangement model[1,2] and demonstrate the fine balance between the dynamic processes leading to rearrangement and deactivation. Of greater importance is the observation that differing cis/trans product ratios from photodissociation of Y from *cis*- and *trans*-$[MA_4XY]$ *does not* preclude the presence of a common set of five-coordinate intermediates. Lastly, initial data on the d^5 Ru(III) systems[9] is compatible with the stereochemical model, although much more experimental work is needed to reinforce this point. However, the fact that the Vanquickenborne/Ceulemans model[1] may be applicable to d^5 systems as well as d^3 and d^6 systems suggests that a unifying concept relating ligand field photosubstitution processes of d^n systems may be emerging.

Kinetic modeling of experimental data utilized a fouth-order Runge–Kutta integration of the rate equations on the Clemson University IBM 370/3033 computer. Initially, either SP_{apical}* or SP_{basal}* was given a unit concentration (all other concentrations were set at zero), and rate constants and reaction times were varied until at least 99% of the initial concentration appeared as ground-state SP_{apical} and SP_{basal}.

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(12) The kinetic treatment applied here can be used to analyze the photochemical reactions of the Co(III) analogues *cis*-$Co(en)_2Cl_2{}^+$ (Sheridan, P. S.; Adamson, A. W. *J. Am. Chem. Soc.* **1974**, *96*, 3032) and *trans*-$Co(en)_2Cl_2{}^+$ (Pribush, R. A.; Poon, C. K.; Bruce, C. M.; Adamson, A. W. *Ibid.* **1974**, *96*, 3027).

Additions and Corrections

1981, Volume 20

M. S. Delaney, C. B. Knobler, and M. F. Hawthorne*: A Designed Metallacarborane Catalyst. Synthesis, Structure, and Reactions of $[closo\text{-}1,3\text{-}[\mu\text{-}(\eta^2\text{-}3\text{-}CH_2{=}CHCH_2CH_2)]\text{-}3\text{-}H\text{-}3\text{-}PPh_3\text{-}3,1,2\text{-}RhC_2B_9H_{10}]$.

Page 1347. In Table VI, under substrate, the second to last entry reads *3,3-dimethylbut-1-ene*. The correct entry should read *3,3-dimethylbut-1-yne*.—M. F. Hawthorne

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1981, Volume 20

Edward H. Wong* and Fontaine C. Bradley: Hydrolysis of Chlorodiphenylphosphine Complexes of Molybdenum and Palladium.

Page 2333. In Table I, the ^{31}P NMR chemical shift for *cis*-$Mo(CO)_4(PPh_2Cl)_2$ should be 126.4 ppm and that for *trans*-$(CO)_4Mo(PPh_2Cl)_2$ should be 137.4 ppm.—Edward H. Wong