continuing our study of this approach with indoles and are extending it to other heterocycles.

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On the Effect of *trans* Ligands on the Rate of Some Bridged Electron-Transfer Reactions[1]

Sir:

In 1956 Orgel[2] suggested that the rates of electron-transfer reactions which go *via* a bridged activated complex should depend on the nature of the group *trans* to the bridging group. Outward motion of the *trans* ligand should facilitate electron transfer by lowering the energy of the orbital which receives the transferred electron.

Using conventional spectrophotometric methods, we have measured the rates of Cr(II) reduction of *cis*- and *trans*-Co(en)₂A(H₂O)⁺³ where en is ethylenediamine and A is either NH_3 or H_2O. In perchlorate media at 7 and 30°, these rates were inversely proportional to [H⁺], which was varied between 0.1 and 1 M. The first acidity constant of each aquo ion was measured by pH titration under similar conditions. The observed [H⁺] dependence indicates that the predominant path for the reaction is an attack of Cr(II) on the conjugate base of the aquo ion. Kruse and Taube[3] have shown that a single oxygen atom is transferred in the Cr(II) reduction of *cis*-Co(en)₂(H₂O)OH⁺²; this supports the bridged electron-transfer mechanism for these reactions.

In Table I our results are listed as the second-order rate constants, k_2, for the Cr(II) reduction of the

Table I. Kinetica Data for Reduction of *cis* and *trans* Aquo and Ammine Bis(ethylenediamine)cobalt(III) Complexes in Perchlorate Media (1 M)

Oxidant	Cr(II) reductant[a] $k_2 \times 10^{-6}$, M^{-1} sec.⁻¹	E_2, kcal./ mole	Fe(II) reductant[b] $k_2 \times 10^4$, M^{-1} sec.⁻¹
cis-Co(en)₂(H₂O)X⁺²	0.79	6.4	4.6
trans-Co(en)₂(H₂O)X⁺²	2.6	2.6	2400
cis-Co(en)₂(NH₃)X⁺²	0.20	5.8	0.18
trans-Co(en)₂(NH₃)X⁺²	0.22	2.4	0.66

[a] X⁻¹ = OH⁻, 25.5°. [b] X⁻ = Cl⁻, 25° (see ref. 4).

hydroxo ions, and the corresponding activation energies, E_2. For comparison, we have listed the recently published results of Benson and Haim[4] on the Fe(II) reductions of the corresponding chloro complexes. The bridge mechanism is a reasonable assumption for the Fe(II) reactions.

The rates of Cr(II) reduction of the Co(en)₂-(NH₃)OH⁺² oxidants are about 10¹⁰ faster than the

(1) Supported by the U. S. Air Force Office of Scientific Research.
(2) L. E. Orgel, *Rept. Xᵉ Consiel, Inst. Intern. Chim. Solvay,* 289 (1956).
(3) W. Kruse and H. Taube, *J. Am. Chem. Soc.,* 82, 526 (1960).
(4) P. Benson and A. Haim, *ibid.,* 87, 3826 (1965).

rates of Fe(II) reductions of the Co(en)₂(NH₃)Cl⁺² oxidants. The principal difference between the two systems resides in the difference of about 1.2 v. (27.6 kcal./mole) in the potentials of the Cr(II) → Cr(III) and Fe(II) → Fe(III) couples. For a pair of outer-sphere electron-transfer reactions for which all factors other than difference in free energy of reaction are either unimportant or constant, Marcus' theory predicts[5]

$$\log \frac{k_{\mathrm{Cr(II)}}}{k_{\mathrm{Fe(II)}}} \approx \frac{1}{2} \frac{\Delta(\Delta F)}{2.303RT} = 10$$

It is interesting that this is the same factor observed for these inner-sphere reactions.

In the Cr(II) reductions, there seems to be no marked correlation of rate with the field strength of the *trans* ligand. The rate of reduction of the *trans* aquo complex is somewhat larger than the other rates in the Cr(II) series, but much larger in the Fe(II) series. This smaller effect implies that outward motion of the *trans* ligand is involved in both cases but is much more important in the slower Fe(II) reductions and agrees with the low isotopic fractionation factor for *trans* nitrogen observed in Co(III)–Cr(II) reductions.[6] Since the activation energies, E_2, are the same for *trans* aquo and *trans* ammine oxidants, the relatively small increase in rate for the Cr(II) reduction of the *trans* aquo species must reside in an entropy effect, possibly involved with partial release of the water molecule into the solvent sheath.

The small but real difference between the activation energies of Cr(II) reductions of oxidants which have a chelated nitrogen atom *trans* to the bridge and those with a monodentate ligand in that position agrees with the suggestion that the chelate attachment restrains motion of the nitrogen atom.[6]

It may be concluded that factors involved with outward motion of the *trans* ligand are not totally absent in the Co(III)–Cr(II) system, but they are much less important than in the Co(III)–Fe(II) reductions which proceed at slower rates because of less favorable free-energy change.

(5) R. Marcus, *J. Chem. Phys.,* 43, 679, (1965); *J. Phys. Chem.,* 67, 853 (1963).
(6) M. Green, K. Shug, and H. Taube, *Inorg. Chem.,* 4, 1184 (1965).

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Photochemistry of Cyclopropylacrylic Esters

Sir:

Current interest in the photochemistry of cyclopropanes[1] prompts us to disclose some preliminary results concerning the photolytic behavior of a cyclopropyl group residing in conjugation with an α,β-unsaturated ester chromophore.

Irradiation[2] of ethyl 3-cyclopropyl-2-butenoate (I)

(1) See, *inter alia:* (a) G. W. Griffin, J. Covell, R. C. Petterson, R. M. Dodson, and G. Klose, *J. Am. Chem. Soc.* 87, 1410 (1965); (b) G. W. Griffin, E. J. O'Connell, and H. A. Hammond, *ibid.,* 85, 1001 (1963); (c) G. S. Hammond, P. Wyatt, C. D. DeBoer, and N. J. Turro, *ibid.,* 86, 2532 (1964); (d) R. C. Cookson, M. J. Nye, and G. Subrahmanyam, *Proc. Chem. Soc.,* 144 (1964); (e) H. E. Zimmerman and D. I. Schuster, *J. Am. Chem. Soc.,* 84, 4527 (1962).
(2) Ether solution, Hanovia 450-w. lamp, and Vycor filter were employed. The benzophenone-sensitized reaction in benzene with Pyrex