of oscillations. The computer shows that the skeleton mechanism requires approximately the increase of R0} with [I03"] that is reflected in the k's of Table I. As proof, compare with these k's the following computed values of and those in column 10, Table II. These are for [IO3"]0 = 0.3 (as opposed to 0.1063) and [H+]0 and [H202]o unchanged.

t, min	1	3	5	7	9	11
10* k	0.304	0.789	1.202	1.415	1.734	1.876
t, min	14	20	40	100	200	260
10*k	1.987	2.01	1.719	1.186	0.820	0.703

At [IO3']0 = 0.3, the "Dushman reversal", previously mentioned, occurs between 3 and 4 min-earlier than in F-16.

The agreement of the k's above with the k's of Table I is all that could be expected, for the k's are average values. The increased Rq2 values following upon [IO3']0 increases exceed what can be directly accounted for by the rates of reactions in which I03~ is consumed. The R0} increases result because the entire reaction system readjusts itself to increasing [IO3"]0, and it is gratifying that the skeleton mechanism provides for this readjustment.

The Skeleton Mechanism Today. This mechanism was designed to be revised as the examination of progressively lectrochemical cells and by direct photolysis.[6,7]

Most of the research of this kind has been concerned with the excited state properties of ruthenium(II)-polypyridyl complexes. In particular, the lowest charge-transfer (CT) excited state of $Ru(bpy)_3^{2+}$ (bpy = 2,2'-bipyridine) has a lifetime of 0.8 ms,[8] reduction potentials for the $Ru(bpy)_3^{2+,/+}$ and $Ru(bpy)_3^{3+/2+*}$ couples are 0.823b and -0.82 V, respectively,[9] and thermodynamically $Ru(bpy)_3^{2+*}$ is capable of reducing water to hydrogen and of oxidizing water to oxygen. Unfortunately, electron transfer to or from the excited state of $Ru(bpy)_3^{2+*}$ has found little direct use except for generating reactive intermediates whose practical applications are limited by their redox potentials or recombination reactions with $Ru(bpy)_3^{+}$ or $Ru(bpy)_3^{3+}$. It is obviously desirable to see if the redox chemistry found for $Ru(bpy)_3^{2+*}$ can be extended to new types of chemical systems both from the fundamental point

Table III. Stern-Volmer Constants and Rate Constants for the Quenching of Ru(TPP)(CO)* by Several Quenchers in (CH3)2SO

quencher	ftf Asv>0 M"1	V M- s'1	k c'M'1 s'1
(1) [TV-ethylphenazonium]4 ion	9.02 X 104	2.50 X 109	1.49 X 10'°
(2) [TV, TV*-dimethyl-4,4'-bipyridinium]24 ion	2.39 X 104	6.64 X 10s	7.75 X 108
(3) [TV-methyl-4-cyanopyridinium] 4 ion	1.22 X 104	3.39 X 10*	3.82 X 10s
(4) [TV-methyl-4-carbomethoxypyridinium]4 ion	7.60	2.11 X 10s	2.11 X 10s
(5) , , ', -tetramethylbenzidine	6.73 X 102	2.02 X 107	2.03 X 107

° Determined using the equation/„// = 1 + A"SV[Q]. All intercepts were very close to 1, correlation coefficients were 0.99 ± 0.01, T= 23 ± 2 °C. 6 fcq was calculated from by using t„[Ru(TPP)(CO)*] = 36.0 gs (Table I, t0'), ± 5%. c Calculated from l/kq = l/kq· + l/kD where kD is the calculated diffusion rate constant, kq is the rate constant for activated quenching, and kq is the measured quenching rate constant.32

X.nm

Figure 1. Difference spectrum at 50 gs following visible flash photolysis of a solution containing 4.2 X "6 M Ru(TPP)(CO) in (CH3)2SO. The triangles show the absorbance decrease following multiple flashes which occurs

TV.TV.jV^TV'-tetramethylbenzidine (Me2NC6H5-C6H5NMe2, TMBZ) was 2.0 X 107 M"1 s'1.

The nature of the quenching process was determined by flash photolysis studies. Paraquat, PQ2+, which is known to quench excited states oxidatively,35 was chosen as a representative example of the first four types of quenchers in Table III. The difference spectrum obtained following flash photolysis of (€113)280 solutions containing Ru(TPP)(CO) and PQ2+ is shown in Figure 2. Qualitatively, the spectrum is exactly what is expected for a composite of Ru(TPP)(CO) bleaching, Ru(TPP)(CO)+ absorbance, and PQ+ absorbance (PQ2+ is transparent in the visible region of the spectrum) based on available spectra in organic solvents.36·37 The back-reaction (eq 1) between PQ+ and Ru-

PQ+

we added 0.28 V to the potentials for the oxidative couples measured in CH2C12.

The second correction makes an energy adjustment for the effect of solvent on the molecular orbitals of the compound. A value of -0.25 V has been derived for this contribution.18a Combining the two correction factors leads to a calculated £ value for Ru(TPP)(CO) of 2.14 V. This is in close agreement to the experimental value of 2.19 V.

The second oxidation may come from either the metal or porphyrin (eq 4 and 5).

Ru"(P+)(CO) RunI(P+)(CO) (4)

Ru“(P+)(CO) Ru“(P2+)(CO) (5)

The difference in potential between the first and second oxidation steps in Table I is 0.42 ± 0.02 V. The potential difference is beyond the range of 0.29 ± 0.05 V found for a series of metalloporphyrins and porphyrins where both oxidations are known to be porphyrin based.44 The pv value of 0.040 V (Figure 3) is also less than the 0.065-V value associated with oxidation at the ring 7r system but may be consistent with oxidation of Ru11 to Rum (eq 4).

When potentials for the Ru(p-XTPP)(CO)2+/+ couples in Table I are analyzed