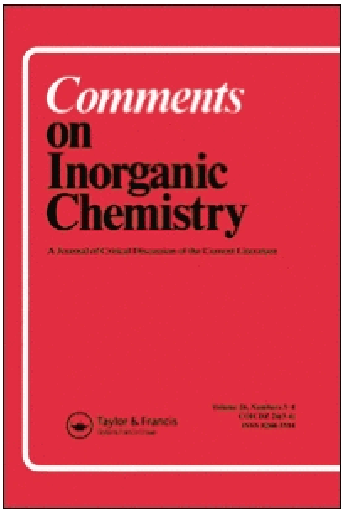

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Bipyridine Radical Ions

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Bipyridine Radical Ions

A survey of the spectral, electrochemical, and chemical properties of organic and inorganic 2,2′-bipyridine (bpy) radical derivatives leads to the conclusion that these species form a common family whose properties are largely determined by those of bpy$^-$, the one-electron reduction product of bpy.

Complexes of 2,2′-bipyridine can be prepared for most metals and, for a given metal center, may persist over a range of oxidation states.[1] The properties of such families as Fe(bpy)$_3^{2+}$, Fe(bpy)$_3^{3+}$ have been extensively studied and have been reviewed.[1,2] It has long been recognized that, in a number of complexes *formally* containing the metal center in a very low oxidation state [e.g., Mg(bpy)$_2^0$], reduced bpy ligand rather than reduced metal center is present {[Mg^{II}(bpy$^-$)$_2$]^0 rather than [Mg^0(bpy)$_2$]^0}.[1,3] In the chromium series, Cr(bpy)$_3^{2+}$ contains Cr(II) and bpy (it is a "normal" complex), but addition of one more electron gives a Cr(III) complex containing two bpy$^-$ ligands. The reduction site (metal or ligand center) is thus not *a priori* obvious and some ingenuity may be required in elucidating the nature of the electronic configurations of these complexes. Recent photochemical efforts have heavily exploited the properties of bpy$^-$ containing ions[4] such as *Ru(bpy)$_3^{2+}$, Ru(bpy)$_3^+$, and purely organic analogues such as the one-electron reduction products of I ("diquat") and of II (methylviologen or paraquat), which is based on the 4,4′-bpy rather than the 2,2′-bpy isomer.

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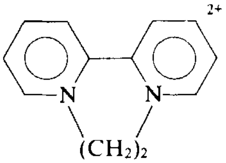
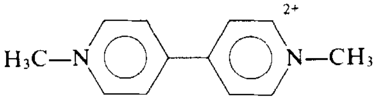


I



II

The understanding of the properties of these species (and in some cases the identification of photochemical intermediates as bpy radical-ion species) has thus attained considerable importance. In this Comment, some of the physical and chemical properties of both "inorganic" and "organic" bpy radical ions, to be denoted BPY^-, will be brought together and compared with the aim of providing an improved understanding of the behavior of both classes.

REDUCTION OF BPY TO BPY^-

The bpy anion $Na^+(bpy^-)$ was made by reaction of sodium metal and 2,2′-bpy in tetrahydrofuran.[5] Although numerous complexes of the type $M(bpy)_2(bpy^-)$, $M(bpy)(bpy^-)_2$, etc., may be made from dilithium 2,2′-bipyridine (which contains the bpy^{2-} anion),[1]

$$y\,Li_2(bpy) + n\,bpy + MX_y \xrightarrow{THF} M(bpy)_n + y\,Li(bpy) + y\,LiX$$

one of the most generally applicable preparative methods is electrochemical reduction. Electrochemical methods also provide detailed information concerning the thermodynamics and kinetics of the reduction of BPY to BPY^- and so such results will be discussed in some detail.

Free 2,2′-bipyridine undergoes reversible one-electron reduction at −2.1 V vs aq SCE in nonaqueous solvents such as acetonitrile and dimethylformamide.[6] The bpy–bpy^- couple thus yields typical one-electron cyclic voltammograms in such media. In metal bpy complexes, the $E_{1/2}$ for the metal couple depends upon the metal ion and, of course, varies widely: contrast $Ru(bpy)_3^{3+/2+}$ + 1.26 V vs NHE in water and $Co(bpy)_3^{2+/1+}$ − 1.0 V vs aq SCE in dimethylformamide. Furthermore, the electrochemical properties of the metal-centered couples (the magnitude of k_s, the value of n, etc.) are a function of the metal center. By contrast, the properties of bound BPY–BPY$^-$ couples follow relatively simple trends.

The successive reduction of tris(2,2′-bipyridine) and tris(1,10-phenanthroline) complexes has been investigated in detail in nonaqueous solvents. Results for the 4d^6 and 5d^6 complexes Ru(bpy)$_3^{2+}$ and Ir(bpy)$_3^{3+}$ provide a useful point of departure.[6,7] Studies of both complexes were carried out at ambient temperature in acetonitrile with platinum electrodes and 0.1 M supporting electrolyte. The behavior found in cyclic voltammetry experiments is shown in Figure 1. For both the Ru(II) and Ir(III) complexes the first three reduc-

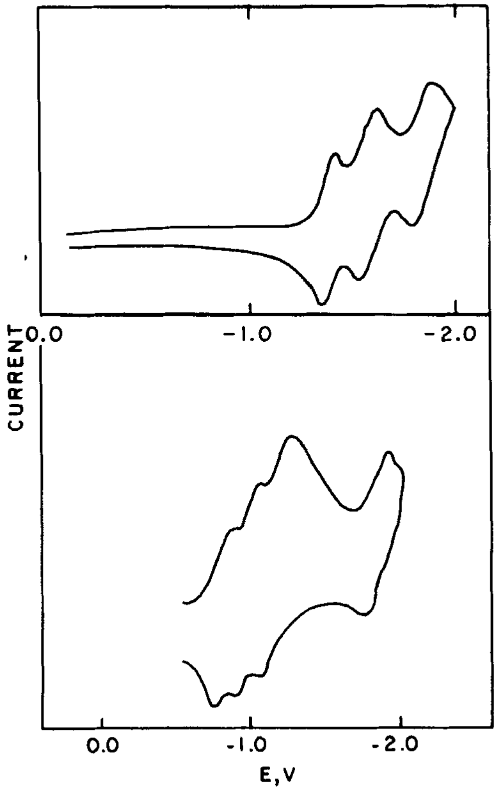


FIGURE 1 Cyclic voltammograms for: *top*, Ru(bpy)$_3^{2+}$ in acetonitrile (E vs a silver reference electrode), adapted from Ref. 6, and *bottom*, Ir(bpy)$_3^{3+}$ in acetonitrile (E vs aqueous SCE), adapted from Ref. 7.

tion steps have been ascribed to electron addition to the ligand as shown in Scheme I, where L denotes the 2,2′-bipyridine ligand and M the Ru(II) or Ir(III) metal center:

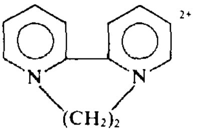
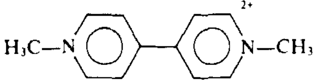
Scheme I

$$ML_3 \underset{-e}{\overset{+e}{\rightleftharpoons}} ML_2(L^-) \underset{-e}{\overset{+e}{\rightleftharpoons}} ML(L^-)_2 \underset{-e}{\overset{+e}{\rightleftharpoons}} M(L^-)_3.$$

For both complexes the spacing between the successive reduction steps is 150 to 200 mV. All three steps are electrochemically reversible over a wide range of sweep rates. The only major difference between the two complexes is in the absolute voltage range in which reduction is observed: reduction of $Ir(bpy)_3^{3+}$ occurs ~0.5 V positive of reduction of $Ru(bpy)_3^{2+}$. This is in accord with the general trend observed for BPY-BPY$^-$ couples as shown in Table I: the reduction potential for the couple becomes more positive when bpy is bound to a cation and, the higher the charge on the cation,

TABLE I

Characteristics of BPY-BPY$^-$ couples on platinum in acetonitrile or dimethyl formamide at room temperature

$E_{1/2}$(I), V[a]		k_s(I), cm s^{-1}	Reference
bpy	−2.13	0.21	6, 8
$bpyH^+$	(⩾−1.55)	···	b, c
$bpyH_2^{2+}$	(⩾−1.21)	···	b, c
$Rh(bpy)_2^+$	−1.43	···	9
$Fe(bpy)_3^{2+}$	−1.26	0.24	8
$Ru(bpy)_3^{2+}$	−1.30	0.24	6, 8
$Os(bpy)_3^{2+}$	−1.18	0.26	8
$Ir(bpy)_3^{3+}$	−0.83	0.3	7
	−0.38[b]	···	10
4,4′-bpy	−1.92	···	11
	−0.45	···	10

[a] Reduction potential vs aqueous SCE.

[b] In aqueous solution, $E_{1/2}$ vs NHE.

[c] Calculated value obtained by assuming $E_{1/2}$ for the bpy-bpy$^-$ couple is −2.13 vs NHE in water and using the pK_a values for bpy and bpy$^-$ reported in Ref. 20.

the more positive the reduction potential. This trend is also illustrated in Figure 2, where $E_{1/2}$ is plotted versus $\bar{Z}$, the charge on the complex divided by the number of bpy groups. Thus, for the series bpy, $Os(bpy)_3^{2+}$ and $Ir(bpy)_3^{3+}$, $E_{1/2}$ for the first reduction peak increases from −2.13 V, to −1.18 V, to −0.83 V, respectively. The data in the table also indicate that, in contrast to the sensitivity to metal charge, the reduction potential is not very sensitive to the identity of the metal center; a range of only 80 mV results on changing from iron to ruthenium to osmium. Furthermore, the heterogeneous electron transfer rate constants k_s for the various BPY–BPY$^-$ couples seem insensitive to the nature of the complex. It is, however, noteworthy that, while lowering the "*metal* center charge" from +3 to +2 [Ir(III) versus Os(II), etc.] shifts the first reduction potential 0.4 to 0.5 V, when the charge of the complex is lowered by the addition of an electron to the *ligand*, the BPY–BPY$^-$ potential shifts only 0.15 to 0.20 V (the peak spacing in Figure 1). Analogous behavior is observed for bis(2,2′-bipyridine) complexes. Thus, for $Rh(bpy)_2^+$ in acetonitrile a pair (rather than a trio) of reduction peaks, separated by 0.19 V, is observed at $E_{1/2} = -1.4$ and

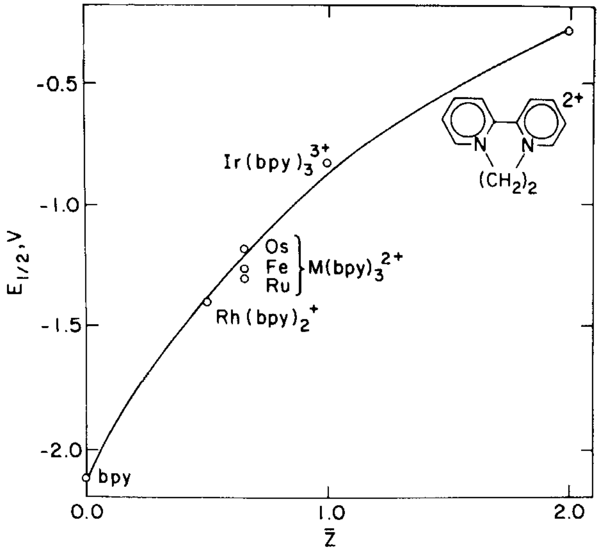
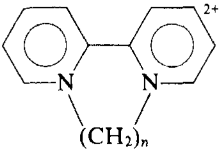


FIGURE 2 Plot of $E_{1/2}$ for BPY–BPY$^-$ couples versus $\bar{Z}$ (the total charge divided by the number of bpy groups).

-1.6 V.[9] The BPY–BPY$^-$ reduction potential is sensitive also to substituents on the bpy ring. This has been extensively documented by Aoyagui and co-workers,[8] who find, for example, that replacement of the 4,4′ hydrogens by methyl groups typically lowers the $E_{1/2}$ about 150 mV. [A similar sensitivity of $E_{1/2}$ to substitution by $-CH_3$ groups is found in the M^{II}–M^{III} potentials for "normal" $M(bpy)_3$ complexes.] Finally, the potentials of the purely organic BPY–BPY$^-$ couples depend, as well, on the nitrogen substituents. For



$E_{1/2}$ drops with increasing alkyl-chain length as follows: $n = 2$, -0.38 V; $n = 3$, -0.49 V; $n = 4$, -0.65 V.[10] This trend is undoubtedly due, in part, to the relative stabilities of six ($n = 2$), seven ($n = 3$) and eight ($n = 4$) membered rings. In addition, the relative orientation of the two pyridine rings (planar or twisted) may affect the degree of delocalization of the added electron in bpy$^-$ and so its reduction potential. Because of the importance of species such as I and II as herbicides and biological electron-transfer mediators, an immense literature concerning the shifts in $E_{1/2}$ with structure exists.[12] Here, however, only a few members of these families need be addressed.

The overall simplicity of BPY–BPY$^-$ electrochemical reduction characteristics over a range of metal centers lends one some confidence that these multiple redox processes may be generally understood in terms of simple successive addition of electrons to uncoupled bpy-centered redox sites whose reducibility is primarily a function of charge. There have, however, recently been disputes as to whether the reduction site in, for example, $M(bpy)_2(bpy^-)$ complexes is localized on one bpy or is instead delocalized over all three[13–15]: this could prove to depend upon M. In addition, in some instances the metal orbitals may be comparable in energy to the lowest occupied molecular orbital in bpy$^-$ so that a less simple picture obtains.[16] These points will be taken up again later.

SPECTRA OF BIPYRIDINE RADICALS

2,2′-Bipyridine manifests two major absorption bands in the UV region. In bpy-containing complexes the higher energy band (~240 nm) is relatively unperturbed, while the longer wavelength band may split and shift according to the charge of the metal center, but in all cases this ligand-centered (π–π^*) transition gives rise to absorption only below ~320 nm.[17] By contrast, the most striking property of BPY$^-$ ions is their color: the reduction of colorless bpy, diquat, paraquat, etc., is accompanied by the growth of blue, green, or violet hues depending upon the BPY used. In general, the reduction leads to π^*–π^* transitions (absent in the spectrum of bpy) and to shifts in the positions of the π–π^* transitions. The former set, which occur at much lower energy than the latter, are responsible for the colors of bipyridine radicals. Observed and calculated spectra for Na$^+$bpy$^-$ have been compared by König and Kremer.[18] The transitions in the visible and near-infrared regions are due to excitation of the ground state ($\phi_1^2\phi_2^2\phi_3^2\phi_4^2\phi_5^2\phi_6^2\phi_7^1$) to configurations such as $\phi_1^2 \cdots \phi_6^2\phi_8^1$ and $\phi_1^2 \cdots \phi_6^2\phi_9^1$ (bands at 750 to 950 nm), $\phi_1^2 \cdots \phi_6^2\phi_{10}^1$ (530–550 nm bands), and $\phi_1^2\phi_2^2\phi_3^2\phi_4^2\phi_5^2\phi_6^1\phi_7^2$ (385 nm band). Hanazaki and Nagakura proposed that the spectra of "low oxidation state" M(bpy)$_3$ complexes could be simply explained in terms of the additive properties of one or more bpy$^-$ chromophores.[3] Recent spectroelectrochemical results of Heath *et al.*[19] confirm this conclusion for the Ru(bpy)$_3^n$, $n = +1$ to -1 series. The general spectral features observed for BPY$^-$ ions are illustrated in Figure 3 where a spectrum of diquat radical is shown. A representative sample of spectral data for BPY$^-$ and BPY$^-$-containing species is given in Table II. Data for the Ru(bpy)$_3$ series illustrate the fact the transitions associated with the M(bpy) (as opposed to the bpy$^-$ chromophore) are retained in the mixed M(bpy)$_2$(bpy$^-$) and M(bpy)(bpy$^-$)$_2$ complexes. For the ruthenium series, this transition is a metal-to-bpy charge-transfer transition occurring at 450 to 485 nm. Aside from such MLCT transitions, the π–π^* and π^*–π^* bpy$^-$-localized bands are the most intense spectral features of bpy$^-$ derivatives and the characteristic three absorption pattern (i.e., 340–390, 450–550, 600–900 nm) provides a useful "fingerprint" for distinguishing the bpy$^-$-containing species.

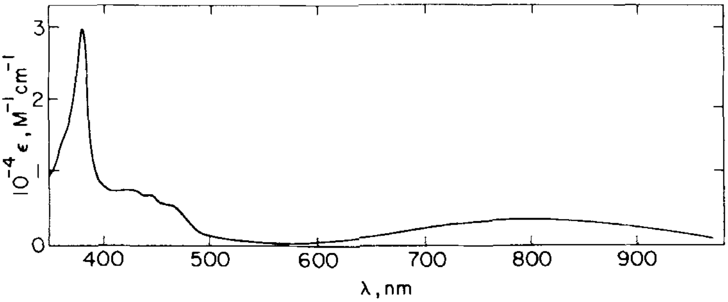


FIGURE 3 The visible-near infrared absorption spectrum of diquat radical I^- in neutral aqueous solution.

EPR spectroscopy has also provided a useful tool for the study of bipyridine radicals. At a relatively elementary level, the presence of a $g \sim 2.00$ resonance indicates the presence of an organic (as opposed to a metal-centered) radical. EPR linewidth studies have also been used to estimate the rate of inter-bpy electron transfer within species such as $[Fe^{II}(bpy)_2(bpy^-)]^+$ to be $> 10^{10}\ s^{-1}$.[15] Vibrational spectroscopy also reveals characteristic differences between bpy and bpy^--containing species. The infrared spectra of "low oxidation state" complexes differ from those of "normal" complexes by the presence of a strong band in the ring deformation region, 1000–900 cm^{-1} [in $Li^+(bpy^-)$ a strong band is seen at 944 cm^{-1}] and by shifts of the intraring C=C and C=N stretching bands in the 1625–1475 cm^{-1} region.[25] The resonance Raman spectra of bpy and Li^+bpy^- and of II and II^- manifest similar trends and, in addition, the stretching frequencies of the inter-ring C–C bonds (1296 cm^{-1} in MV^{2+}) are found to increase upon radical formation (1350 cm^{-1} in MV^+).[26,27] The shifts for II/II^- have been compared to those encountered for the parent hydrocarbon pair biphenyl/biphenyl negative ion. For the latter the shifts were also attributed to increased inter-ring bonding. The π-bond order changes implicated for the hydrocarbon upon radical ion formation are as follows[28]:

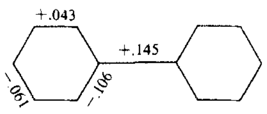


TABLE II

Absorption spectra of bpy and bpy^--containing species

	λ_{max}, nm ($10^{-4}\epsilon$, $M^{-1}\,cm^{-1}$) $\pi-\pi^*$ bpy	$\pi-\pi^*$ bpy^-	M → L bpy	$\pi^*-\pi^*$ bpy^-	$\pi^*-\pi^*$ bpy^-	Ref.
bpy^{a}	235 280(1.4)	···	···	···	···	17
$Na^+(bpy^-)$–THF	···	386(2.95)	···	532(0.62) 562(0.65)	752(0.11) 833(0.15) 952(0.13)	18
$bpyH^{+a}$	302(1.5)	···	···	···	···	20
$bpyH\cdot^{a}$	···	360(2.9)	···	450(1.4)	630(0.15)	20
$bpyH_2^{2+a}$	290(1.5)	···	···	···	···	20
$bpyH_2\cdot^{+a}$	···	375(4.5)	···	430(0.7)	800(0.3)	20
$bpy(CH_2-)_2^{2+}(I)^{a}$	310(1.9)	···	···	···	···	21
$bpy(CH_2-)_2\cdot^+(I^-)^{a}$	···	377(3.0)	···	440(1.2) 460(0.9)	740(0.6)	22, 23
$Ru(bpy)_3^{2+b}$	285(7.8)	···	454(1.4)	···	···	19
$[Ru(bpy)_2(bpy^-)]^{+b}$	292(4.4)	342(1.4)	474(1.0)	503(1.1)	781, 870, 990	19
$[Ru(bpy)(bpy^-)_2]^{0b}$	296(3.5)	345(2.3)	481(sh)	529(1.0) 513(1.2) 543(1.2)	787, 900, 1000	19
$4,4'\text{-}bpy^{-a,c}$	365(3.7)	···	545(1.2)	···	···	24
$4,4'\text{-}bpyH\cdot^{a,c}$	···	385(3.8)		570(1.3)	···	24
$(CH_3)_2\text{–}4,4'\text{-}bpy\cdot^+(II^-)^{a}$	···	393(3.4)	···	605(1.2)	···	12

[a] Aqueous solution.

[b] Acetonitrile solution.

[c] By contrast to the aqueous 2,2′-bpy system, for which the pK_a for $bpyH \rightleftharpoons bpy^- + H^+$ is >14 [20], the pK_a for the corresponding para isomer is 10.5.[24]

An immense range of reactivities is observed for bipyridine radicals in aqueous solution in the absence of added oxidants or reductants (or platinum catalysts). Electrolytically reduced diquat(I) persists for weeks (or more) at neutral pH so long as O_2 is excluded.[23] By contrast, at neutral pH the lifetimes of bpyH and $bpyH_2^+$ produced at micromolar levels in pulse radiolysis experiments lie in the millisecond time range.[20] The reactivity of metal-bound BPY^- appears to lie between these two extremes. For example, $Ru(bpy)_3^+$ has a lifetime of 5 s at pH 11–13.[29] Since the pathway responsible for rapid destruction of bpyH (and $bpyH_2^+$) is an extremely rapid dismutation reaction[20]

$$2\ \mathrm{bpyH} \rightarrow \mathrm{bpy} + \mathrm{bpyH_2} \tag{1}$$

apparently absent in the other systems, it is worth considering thermodynamic data bearing on dismutation of BPY in seeking an explanation for the marked reactivity contrasts. Data relevant to oxidation of BPY^- to BPY were presented in Table I. We now consider data bearing on the BPY^-/BPY^{2-} couple. In all the systems for which data are available, $E_{1/2}(\mathrm{II})$ for this couple, i.e.,

$$\mathrm{BPY^-} + e^- = \mathrm{BPY^{2-}} \qquad E_{1/2}(\mathrm{II}) \tag{2}$$

lies negative of $E_{1/2}(\mathrm{I})$. That is, dismutation of species such as *un*protonated bpy, diquat, etc., is *not* thermodynamically favorable. From the values of $E_{1/2}(\mathrm{I})$ and $E_{1/2}(\mathrm{II})$, the magnitude of the equilibrium constant for dismutation

$$2\ \mathrm{BPY^-} \xrightleftharpoons{K_{\mathrm{dis}}} \mathrm{BPY} + \mathrm{BPY^{2-}} \tag{3}$$

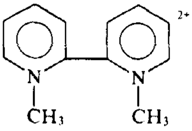
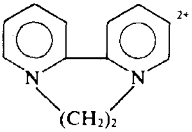
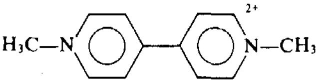
can be calculated. Values for K_{dis}, as well as $E_{1/2}(\mathrm{I})$ and $E_{1/2}(\mathrm{II})$, are presented in Table III. While $E_{1/2}(\mathrm{II})$ is not known for bpy, the fact that $K_{\mathrm{dis}} < 1$ in solvents such as acetonitrile and dimethyl formamide can be deduced from the fact that a *one*-electron reversible reduction is observed. For the bis- and tris-bpy metal complexes Eqs. (4) and (5) occur, rather than Eqs. (2) and (3), since the "second" reduction site is bpy rather than bpy^-:

$$\mathrm{M(bpy)_2(bpy^-)} + e^- = \mathrm{M(bpy)(bpy^-)_2} \qquad E_{1/2}(\mathrm{II}), \tag{4}$$

$$2\ \mathrm{M(bpy)_2(bpy^-)} \xrightleftharpoons{K'_{\mathrm{dis}}} \mathrm{M(bpy)_3} + \mathrm{M(bpy)(bpy^-)_2}. \tag{5a}$$

TABLE III

Stabilities of bipyridine radicals with respect to dismutation

	$E_{1/2}$(I), V[a]	$E_{1/2}$(II), V[a]	K_{dis}	Ref.
bpy	-2.13	<-2.2	$<10^{-1}$	6
	-0.68	-0.75	5×10^{-2}	12
	-0.34	-0.82	1×10^{-8}	12
$Ru(bpy)_3^{2+}$	-1.30	-1.49	6×10^{-4}	6
$Ir(bpy)_3^{3+}$	-0.83	-1.00	1×10^{-3}	7
4,4′-bpy	-1.92	<-2.0	$<10^{-1}$	11
4,4′-bpyH_2^{2+}	...	...	1×10^{-12}[b]	12
	-0.45[c]	-0.88[c]	5×10^{-8}	12

[a] $E_{1/2}$ with respect to aq SCE in acetonitrile unless otherwise stated.

[b] In methanol.

[c] In aqueous solution, $E_{1/2}$ vs NHE.

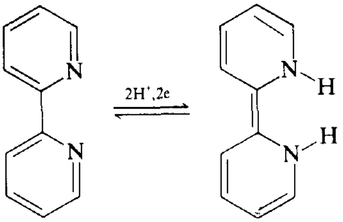
For such couples K'_{dis} is again less than unity, as is evident from Figure 1: The 0.15 to 0.2 V spacing between the one-electron peaks in the cyclic voltammograms of $Ru(bpy)_3^{2+}$ and $Ir(bpy)_3^{3+}$ leads to K_{dis} values $\leqslant 10^{-2}$ as shown in Table III. Note also that the process

$$M(bpy)(bpy^-)_2 \rightleftharpoons M(bpy)_2(bpy^{2-}) \qquad (5b)$$

must be included with Eqs. (4) and (5a) for the process to be strictly analogous to that [Eqs. (2), (3)] for metal-free BPY^-.

Thus dismutation of BPY^- via Eq. (3) or (5) is not generally favored and the reactivity of bpy^- with respect to dismutation in *aqueous* solutions [Eq. (1)] is probably a consequence of its protonation and of the possibility of forming the "protonated" product $bpyH_2$. The impetus for this reaction is clarified to some extent by studies of the electroreduction of bpy (or M^+bpy with $M^+ = Na^+, K^+, Li^+$)

at pH 12–14. Chemically reversible, two-electron reduction of bpy was observed at $E = -1.34$ V vs NHE.[30] A mixture of equilibrated



isomeric dihydrobipyridines was produced, but the first (and least stable) to be formed was the isomer shown. From the reversible potential at which reduction was observed at high pH the E^0 for Reaction (6) can be estimated as −0.64 V:

$$\text{bpy} + 2\text{H}^+ + 2\text{e}^- = \text{bpyH}_2 \qquad (6)$$

From the pK_a data for bpy (bpyH$^+$/bpy pK_a 4.25, bpyH$_2^{2+}$/bpyH$^+$ pK_a −0.2) and bpy$^-$ (bpyH/bpy$^-$ p$K_a \geqslant 14$, bpyH$_2^+$/bpyH pK_a 5.6) given in Ref. 20 and the one-electron reduction potentials given in Table I, the dismutation equilibrium constants for Eqs. (1) and (7) are estimated as $\geqslant 10^{29}$ and $\geqslant 10^{23}$, respectively:

$$2\ \text{bpyH} \rightleftharpoons \text{bpy} + \text{bpyH}_2, \qquad (1)$$

$$2\ \text{bpyH}_2^+ \rightleftharpoons \text{bpyH}_2^{2+} + \text{bpyH}_2. \qquad (7)$$

[Here Eq. (7) is included, even though it is hardly relevant above pH 0, because it has the symmetry of Eq. (3).] The very large instability of bpyH and pbyH$_2^+$ with respect to dismutation is due *not* to the bpyH$^+$/bpyH or bpyH$_2^{2+}$/bpyH$_2^+$ reduction potentials ($\geqslant -1.55$ and $\geqslant -1.21$ V, respectively) which are quite unremarkable, but rather to the bpyH$_2^+$/bpyH$_2$ reduction potential which is +0.17 V.

These considerations confirm the role of protons and protic solvents in limiting the longevity of bpy$^-$ radicals and suggest that it is the stability and ease of formation of the *N,N′*-dihydrobipyridine which drives dismutation reactions such as (1) and (7). BPY$^-$ radical species such as diquat radical cannot undergo analogous reactions in water because the nitrogens, the sites most rapidly protonated, are blocked. Thus any dianion BPY^{2-} formed through the unfavorable Eqs. (3) and (5) could only be carried on to protonated product (a substituted dihydrobipyridine) via inherently slow protonation of carbon. Finally, it is not unlikely that the stability of some $M(bpy)_2(bpy^-)$ species may be limited by a pathway not yet discussed. Intramolecular electron transfer, Eq. (8),

$$M^n(bpy)_2(bpy^-) \rightleftharpoons M^{n-1}(bpy)_2(bpy) \tag{8}$$

may lead to release and reduction of bpy, Eqs. (9), (10), and subsequent reactions such as Eq. (1) would result in net decomposition of

$$M^{n-1}(bpy)_2(bpy) \xrightleftharpoons{H_2O} M^{n-1}(bpy)_2(H_2O)_2 + bpy, \tag{9}$$

$$M^{n-1}(bpy)_2(H_2O)_2 + bpy \xrightleftharpoons{H^+} M^n(bpy)_2(H_2O)_2 + bpyH, \tag{10}$$

$M^n(bpy)_2(bpy^-)$ and formation of $bpyH_2$. Reactions producing H_2 are also possible. As is evident from Table I, BPY^- radicals are generally thermodynamically capable of water reduction

$$BPY^- + H_2O \rightarrow BPY + \tfrac{1}{2} H_2 + OH^-$$

over a wide pH range. This is, in fact, the origin of much of the current focus on BPY^- chemistry. Despite the thermodynamic favorability of this reaction, it is so far known to occur only in the presence of heterogeneous catalysts (colloidal platinum, PtO_2, etc.) and in the system[31]

$$Ru(bpy)(bpy^-)_2^0 + 2\,H_2O \rightarrow Ru(bpy)_3^{2+} + 2\,OH^-.$$

One of the most extensively exploited features of the BPY–BPY^- couples is their high reactivity toward outer-sphere electron-transfer reactions. The rate constants for such reactions, i.e., Eq. (11),

$$D + BPY \rightleftharpoons D^+ + BPY^- \tag{11}$$

are a function of the driving force for the reaction and of the intrinsic reactivity of the BPY–BPY^- and D–D^+ couples. The former is obtained from the difference between the redox potentials for the two couples and the data in Table I are relevant in this context. The latter is reflected in the magnitude of the rate constant for the self-exchange reaction, Eq. (12):

$$BPY^- + BPY \rightleftharpoons BPY + BPY^-. \tag{12}$$

Rate constants for BPY–BPY^- exchanges are expected to be relatively large because the barrier associated with the electron transfer is small: when an electron is added to (or removed from) ϕ_7, the lowest unoccupied orbital of BPY, only small changes in the C–C, C–N, and C–H bond lengths and vibrational frequencies ensue. The major contribution to this "inner shell" electron transfer barrier, the IR and resonance Raman studies suggest, derives from changes in the inter-ring C–C bond (2,2′ in 2,2′-bpy, 4,4′-bpy). In addition, the outer-shell barrier to the electron exchange is expected to be modest since the BPY–BPY$^-$ species are relatively large. These expectations are largely borne out by experiment. Exchange rate estimates for metal-bound couples such as Ru(bpy)$_2$-(bpy$^-$)$^+$–Ru(bpy)$_3^{2+}$ exceed 10^8 M^{-1} s^{-1} [32] (25 °C, aqueous solution, $\mu = 0.1$–1.0 M) while those obtained for the organic analogues are somewhat smaller, being $(0.5$–$2.0) \times 10^6$ M^{-1} s^{-1} [10,33] under comparable conditions. The lower rates for the organic species such as paraquat and diquat may be due to a greater outer-shell barrier stemming from the smaller reactant size.

CURRENT PROBLEMS

Much of the present effort in the areas of inorganic photochemistry and solar energy storage research derives from the properties of *Ru(bpy)$_3^{2+}$, the lowest excited state of Ru(bpy)$_3^{2+}$. Crosby and coworkers described this excited state as a metal-to-ligand charge-transfer (MLCT) excited state on the basis of photophysical and spectroscopic results,[34] but it has been the spectral and chemical experiments in solution at ambient temperature which have given substance to the description of this species as the metal-bound bipyridine radical Ru^{III}(bpy)$_2$(bpy$^-$)$^{2+}$. This species and its heavier congener Os^{III}(bpy)$_2$(bpy$^-$)$^{2+}$ manifest the characteristic BPY$^-$ π–π^* and π^*–π^* transitions in the near UV and visible regions[32]: λ_{max} 360 nm ($\epsilon = 1.3 \times 10^4$ M^{-1} cm^{-1}) and 430 nm ($\epsilon = 0.6 \times 10^4$ M^{-1} cm^{-1}) for *Ru(bpy)$_3^{2+}$ and λ_{max} 360 nm ($\epsilon = 1.8 \times 10^4$ M^{-1} cm^{-1}) and 460 nm ($\epsilon = 0.5 \times 10^4$ M^{-1} cm^{-1}) for *Os(bpy)$_3^{2+}$. The fact that *Fe(bpy)$_3^{2+}$, the lowest excited state of Fe(bpy)$_3^{2+}$, exhibits no such low energy spectral features is taken as evidence that the latter is a ligand field rather than an MLCT excited state.[4] Recent resonance Raman results for ground and excited Ru(bpy)$_3^{2+}$ reveal the characteristic shifts in C–C and C–N frequencies discussed above for bpy/bpy and paraquat/paraquat radical. Namely, excitation of $Ru(bpy)_3^{2+}$ leads to an increase in the 2,2′ C–C stretching frequency and to other shifts seen in the ground-state BPY^- species.[14,26,35] Such experiments have recently led to a revision of the description of $^*Ru(bpy)_3^{2+}$. Whereas it had earlier been described in terms of a Ru(III) core surrounded by a $(bpy)_3^-$ core (electron delocalized over all three ligands) the Raman work implicates the localized description $Ru^{III}(bpy)_2(bpy^-)^{2+}$.

To consider another aspect of the properties of these species—the redox potential for the $Ru(bpy)_3^{3+}/{}^*Ru(bpy)_3^{2+}$ couple was originally calculated from ground-state spectroscopic and thermodynamic properties[36] and confirmed by experimental measurements to be −0.84 V vs NHE in water at 25°C. From the potential data in Table I and Figure 1 it is now apparent that this is the value which would have been estimated by considering the equation

$$Ru^{III}(bpy)_3^{3+} + e^- = [Ru^{III}(bpy)_2(bpy^-)]^{2+}, \qquad (13)$$

that is, by formulating the question "what is the bpy–bpy^- potential when bpy is bound to a 3+ metal center?" In fact, if we assume the potentials of presently unknown $M^{III}(bpy)_3/M^{III}(bpy)_2(bpy^-)$ couples can be estimated from Table I and Figure 1, we can turn the calculation around and estimate excited-state energies for uncharacterized $M(bpy)_3^{2+}$ MLCT excited states. These are obtained from the cycle

$$M^{III}(bpy)_3^{3+} + e^- \rightleftharpoons M(bpy)_3^{2+}, \qquad (14)$$

$$M^{III}(bpy)_3^{3+} + e^- \rightleftharpoons M^{III}(bpy)_2(bpy^-), \qquad (15)$$

$$M(bpy)_3^{2+} \rightleftharpoons M^{III}(bpy)_2(bpy^-), \qquad (16)$$

where $M^{III}(bpy)_2(bpy^-)$ is $^*M(bpy)_3^{2+}$, the MLCT excited state of $M(bpy)_3^{2+}$, and the free energy change for Eq. (16) gives E^*, the excitation energy of (thermally equilibrated) $^*M(bpy)_3^{2+}$. For $^*Ru(bpy)_3^{2+}$, $E^* = 2.08$ eV.[4] From Eqs. (14)–(16) [taking the E^0 for Eq. (15) to be −0.85 V] E^* is estimated as 1.95 eV for $^*Fe(bpy)_3^{2+}$, 1.2 eV for $Co(bpy)_3^{2+}$, and 0.5 V for $Cr(bpy)_3^{2+}$. Depending upon M, the MLCT excited state may or may not be relevant to the photochemistry (if any) observed for $M(bpy)_3^{2+}$. Such indirect estimates of excited-state energies may, however, prove useful in obtaining a total picture of the excited state manifolds in these and other systems.

In short, the work done so far indicates that the $\mathrm{M(bpy)_2(bpy^-)}$ description of $\mathrm{{*}Ru(bpy)_3^{2+}}$ and other MLCT states is a useful and realistic one. Of course, a number of interesting and important questions remain to be answered. Among others, what is the lifetime of a given $\mathrm{bpy^-}$ in $\mathrm{Ru^{III}(bpy)_2(bpy^-)}$, i.e., how rapid is inter-bpy electron exchange in this and related species such as $\mathrm{Ru(bpy)_3^+}$? A related unanswered question concerns the absorption and emission spectra of $\mathrm{Ru(bpy)_3^{2+}}$. Both (as well as the excited-state lifetime) are essentially solvent independent.[37] How can this be reconciled with the $\mathrm{Ru^{III}(bpy)_2(bpy^-)^{2+}}$ description of the excited state? This formulation requires a change in dipole moment upon excited-state formation—thus leading to the expectation of solvent dependent spectra.

A major challenge to our understanding of the behavior of "low oxidation state" bpy complexes is posed by the properties of $\mathrm{Rh(bpy)_3^{2+}}$.[16] The latter [like $\mathrm{{*}Ru(bpy)_3^{2+}}$] exists only as a transient in flash photolysis and pulse radiolysis experiments, but a rather comprehensive picture of its chemical and some of its physical properties has emerged. The $\mathrm{Rh(bpy)_3^{3+}/Rh(bpy)_3^{2+}}$ potential, -0.86 V vs NHE in water, is consistent with its formulation as a $\mathrm{BPY^-}$ complex (see Table I and Figure 1). Its self-exchange rate ($>10^9$ $\mathrm{M^{-1}\,s^{-1}}$) is also consistent with this model—but the spectrum of $\mathrm{Rh(bpy)_3^{2+}}$ lacks the intense near UV and visible features expected (see Table II). Instead $\epsilon_{360} = 0.4 \times 10^4\ \mathrm{M^{-1}\,cm^{-1}}$ and $\epsilon_{490} = 0.1 \times 10^4\ \mathrm{M^{-1}\,cm^{-1}}$. Furthermore, the substitution lability of the species is orders of magnitude greater than expected for a rhodium(III) metal center. These observations appear to require either the delocalized description A

$$\text{A: } \mathrm{Rh^{II}(bpy)_3^{2+}} \leftrightarrow \mathrm{Rh^{III}(bpy)_2(bpy^-)^{2+}}$$

or the equilibrium description B [note that B is the reverse of Eq. (8)]:

$$\text{B: } \mathrm{Rh^{II}(bpy)_3^{2+}} \overset{K_B}{\rightleftharpoons} \mathrm{Rh^{III}(bpy)_2(bpy^-)}.$$

In the equilibrium description, $\mathrm{Rh^{II}(bpy)_3^{2+}}$ is written as the dominant form to account for the spectrum. In fact, on the basis of the observed band intensities $K_B < 10^{-1}$. Definitive evidence ruling out or confirming description A or B is presently lacking. It is interesting, however, to note that the electronic isomerism B finds its precedent in the Class II mixed-valence ions and in the spin equilibrium systems. While a barrier to the interconversion of the two forms exists by virtue of the energy difference between them and because of their different nuclear configurations, the interconversion rates are likely to be quite rapid, probably greater than 10^7 s^{-1}. Here [as with $Ru(bpy)_3^{2+}$ and $Os(bpy)_3^{2+}$] the BPY^- form would be an excited state of the complex—but a thermally accessible one. In passing, we note that an analogous ambiguity arises in the description of $Re(phen)(CO)_3L^0$ (L = pyridine or triphenylphosphine). This nominal Re^0 complex is extremely substitution labile but is postulated to possess substantial $phen^-$ character.[38]

We have seen that organic and inorganic bipyridine radicals possess many common features: The characteristic three-band absorption features in the near UV, visible and near-infrared region are relatively insensitive to the chemical environment of BPY^-. The shifts in vibrational frequencies that occur when BPY is reduced to BPY^- are similarly insensitive to environment. The reduction potentials of BPY–BPY^- couples are largely a function of charge. With the exception of free bpy^- in aqueous solution, BPY^- species are rather stable so long as oxidants are excluded. The chemistry of many of the inorganic systems may, however, possess an added dimension in that intramolecular electron transfer [Eq. (8)] yields a low oxidation state of the metal center. To date, reactions of this sort have been noted largely only because of their negative aspects; they generally lead to decomposition. Nonetheless, in the future it could be that such processes will be deliberately exploited as a controlled source of reactive low oxidation state metal complexes. An additional important future direction in the metal-bound BPY^- chemistry is the use of such materials as multiequivalent reductants. This was exploited by Abruna *et al.*[31] in work in which $Ru(bpy)(bpy^-)_2^0$ [but not the one-electron reductant $Ru(bpy)_2(bpy^-)^+$] was shown to rapidly and stoichiometrically reduce water to H_2, with $Ru(bpy)_3^{2+}$ being the oxidized product. Species such as $M(bpy)(bpy^-)_2$ and $M(bpy^-)_3$ provide potential multiequivalent reductants with the differences in redox potentials for the various oxidation steps being rather modest. Certainly this is an area worthy of further effort. In short, there seems much room for interesting developments in the chemistry of the inorganic BPY^- derivatives.

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References

1. W. R. McWhinnie and J. D. Miller, Adv. Inorg. Chem. Radiochem. **12,** 135 (1969).
2. P. Krumholz, Struct. Bonding **9,** 139 (1971).
3. I. Hanazaki and S. Nagakura, Bull. Chem. Soc. Jpn. **44,** 2312 (1971).
4. N. Sutin and C. Creutz, Pure Appl. Chem. **52,** 2717 (1980); V. Balzani, F. Bolletta, M. T. Gandolfi and M. Maestri, Top. Curr. Chem. **1978,** 1 (1978).
5. C. Mahon and W. L. Reynolds, Inorg. Chem. **6,** 1927 (1967).
6. N. E. Tokel-Takvoryan, R. E. Hemingway and A. J. Bard, J. Am. Chem. Soc. **95,** 6582 (1973).
7. J. L. Kahl, K. W. Hanck and K. DeArmond, J. Phys. Chem. **82,** 540 (1978).
8. T. Saji and S. Aoyagui, J. Electroanal. Chem. **63,** 31 (1975).
9. G. Kew, K. DeArmond and K. Hanck, J. Phys. Chem. **78,** 727 (1974).
10. E. Amouyal, B. Zidler, P. Keller and A. Moradpour, Chem. Phys. Lett. **74,** 314 (1980).
11. K. B. Wiberg and T. P. Lewis, J. Am. Chem. Soc. **92,** 7154 (1970).
12. See, for example, S. Hunig and H. Berneth, Top. Curr. Chem. **92,** 1 (1980) and C. L. Bird and A. T. Kuhn, Chem. Soc. Rev. **10,** 49 (1981).
13. G. A. Crosby and W. H. Elfring, Jr., J. Phys. Chem. **80,** 87 (1976).
14. P. G. Bradley, N. Kress, B. A. Hornberger, R. F. Dallinger and W. H. Woodruff, submitted for publication.
15. A. G. Motten, K. Hanck and M. K. DeArmond, Chem. Phys. Lett. **79,** 541 (1981).
16. C. Creutz, A. D. Keller, H. A. Schwarz, N. Sutin and A. P. Zipp, Adv. Chem. Ser., in press.
17. B. Martin, W. R. McWhinnie and G. M. Waind, J. Inorg. Nucl. Chem. **23,** 207 (1961).

18. E. König and S. Kremer, Chem. Phys. Lett. **5,** 87 (1970).
19. G. A. Heath, L. J. Yellowlees and P. S. Braterman, J. Chem. Soc. Commun. **1981,** 287 (1981).
20. Q. G. Mulazanni, S. Emmi, P. G. Fuochi, M. Venturi, M. Z. Hoffman and M. G. Simic, J. Phys. Chem. **83,** 1502 (1979).
21. R. F. Homer and T. E. Tomlinson, J. Chem. Soc. **1960,** 2498 (1960).
22. E. Steckhan and T. Kuwana, Ber. Bunsenges. Phys. Chem. **78,** 253 (1974).
23. A. Keller, unpublished observations.
24. M. Simic and M. Ebert, Int. J. Radiat. Phys. Chem. **3,** 259 (1971).
25. Y. Saito, J. Takimoto, B. Hutchinson and K. Nakamoto, Inorg. Chem. **11,** 2003 (1972).
26. M. Forster and R. E. Hester, Chem. Phys. Lett. **81,** 42 (1981).
27. P. C. Lee, K. Schmidt, S. Gordon and D. Meisel, Chem. Phys. Lett. **80,** 242 (1981).
28. C. Takahashi and S. Maeda, Chem. Phys. Lett. **24,** 584 (1974).
29. Q. G. Mulazanni, S. Emmi, P. G. Fuochi, M. Z. Hoffman and M. Venturi, J. Am. Chem. Soc. **100,** 981 (1978).
30. H. Erhard and W. Jaenicke, Elecroanal. Chem. **81,** 89 (1977).
31. H. D. Abruna, A. Y. Teng, G. J. Samuels and T. J. Meyer, J. Am. Chem. Soc. **101,** 6745 (1979).
32. N. Sutin and C. Creutz, Adv. Chem. Ser. **168,** 1 (1978).
33. C. R. Bock, J. A. Connor, A. R. Gutierrez, T. J. Meyer, D. G. Whitten, B. P. Sullivan and J. K. Nagle, J. Am. Chem. Soc. **101,** 4815 (1979).
34. G. D. Hager, R. J. Watts and G. A. Crosby, J. Am. Chem. Soc. **97,** 7037 (1975).
35. R. F. Dallinger and W. H. Woodruff, J. Am. Chem. Soc. **101,** 4393 (1979).
36. G. Navon and N. Sutin, Inorg. Chem. **13,** 2159 (1974).
37. C. Creutz and N. Sutin, unpublished work.
38. D. P. Summers, J. C. Luong and M. S. Wrighton, J. Am. Chem. Soc. **103,** 5238 (1981).