Photocatalysis of the Pschorr Reaction by Tris-(2,2′-bipyridyl)ruthenium(II) in the Phenanthrene Series

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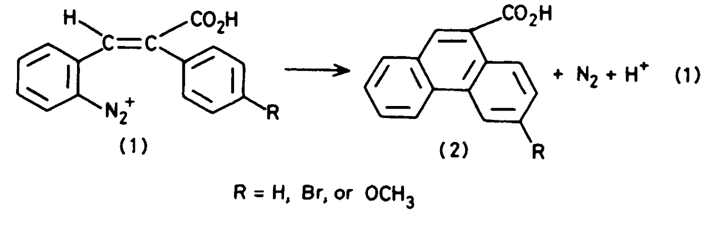
The photocatalytic conversion of the tetrafluoroborate salt of the stilbenediazonium ion (1) into the corresponding phenanthrene (2) (Pschorr reaction) by $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridyl) has been investigated. We have shown that this particular Pschorr reaction takes place quantitatively with a high quantum yield ($\varphi > 0.4$) upon selective photoexcitation of a catalytic amount of $Ru(bpy)_3^{2+}$. Quenching and conventional flash photolysis experiments have revealed that quenching of the excited state of $Ru(bpy)_3^{2+}$ probably occurs by an electron-transfer process. In contrast it has been shown that direct photolysis of (1) leads to the Pschorr reaction with a poorer yield (10–20%).

The excited states of ruthenium complexes with polypyridyl ligands such as $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridyl) have attracted intense interest in recent years, especially in terms of applications to problems in photoredox catalysis.[1] Most of the investigations have been related to the photocatalytic splitting of water into H_2 and O_2 or the production of other small molecules such as H_2O_2 or halogens. A large number of homogeneous and heterogeneous catalysed systems and photoelectrochemical cell applications have been described, based on $Ru(bpy)_3^{2+}$.[1] Curiously, however, only a few examples have appeared which take advantage of $Ru(bpy)_3^{2+}$ photoredox properties in organic chemistry.[2–7] In this paper we report the utilization of $Ru(bpy)_3^{2+}$ as photocatalyst for the Pschorr reaction, especially in the phenanthrene series. Pschorr and Pschorr-like reactions [*e.g.* equation (1) in the phenanthrene series] involve intramolecular arylation upon reduction of the appropriate diazonium salt by a reducing agent, by electrochemical reduction, or by simple heating.[8] We have found that the Pschorr reaction (1) takes place quantitatively with a high quantum yield ($\varphi > 0.4$) upon selective photoexcitation of a catalytic amount of $Ru(bpy)_3^{2+}$ and that the reaction proceeds, at least in part, by a photoinduced electron-transfer process.

Experimental

Materials.—The diazonium tetrafluoroborate (1) was prepared from the corresponding 2-amino-α-arylcinnamic acid by a standard procedure.[9] It was purified by dissolving three times in acetonitrile followed by precipitation with anhydrous ether and dried overnight. The solid was stored under vacuum at 0 °C. 2-Amino-α-arylcinnamic acids were prepared from the corresponding 2-nitro-α-arylcinnamic acid using the general procedure described in the literature.[10] 2-Nitro-α-arylcinnamic acid was synthesised from *o*-nitrobenzaldehyde and the corresponding substituted phenylacetic acid by a classical Perkin condensation.[11] The phenanthrene (2) used for h.p.l.c. analysis was prepared by reduction of (1) by tetraethylammonium iodide and purified as described in ref. 8. The acetamide derivatives (3) were prepared from 2-amino-α-arylcinnamic acid by action of glacial acetic acid and acetic anhydride as reported previously.[12] Their structures were verified by mass spectrometry, (3; R = H) m/z 281 (38%, $M^{\cdot+}$), 222, 220, 194, 193, and 43; (3; R = CH_3) m/z 311 (34%, $M^{\cdot+}$), 252, 251, 224, 117, and 43; and (3; R = Br) m/z 359 (19%, $M^{\cdot+}$), 300, 274, 272, 193, and 43. 4-Bromobenzenediazonium tetrafluoroborate was prepared and purified by a standard procedure.[13] $Ru(bpy)_3^{2+}(BF_4^-)_2$ and the ligand-modified complex (6) as the PF_6^- salt were prepared as previously reported in the literature.[4a,14] Acetonitrile and tetrabutylammonium perchlorate were purified as described elsewhere.[15]

Spectra and Analysis.—All electronic spectra and routine i.r. spectra were recorded on Beckman Acta IV and Beckman 4240 spectrophotometers, respectively. Luminescence quenching measurements were performed with a Jobin Yvon JY3C fluorescence spectrophotometer. Stern–Volmer intensity quenching experiments were carried out using argon-degassed solutions. Six different concentrations of quenchers were used ranging from zero to that resulting in *ca.* 80% quenching. Using the Stern–Volmer relationship $I_0/I = 1 + k_q\tau_0[Q]$ where k_q is the quenching rate constant, τ_0 the life-time of the excited state, plots of I_0/I against [Q] permit k_q to be determined. I_0/I was corrected for light absorption by the quencher for R = OCH_3 according to ref. 16. Conventional flash photolysis experiments were performed using a modified Nortech EPX-1 device. A Nicolet Explorer III storage oscilloscope was used for data acquisition. Cyclic voltammograms were obtained by using a PAR model 173 potentiostat and a PAR 175 universal programmer. All potentials were reported *versus* the aqueous saturated calomel electrode (s.c.e.). H.p.l.c. analyses were performed with a Waters Associates Instruments high performance liquid chromatograph (on a 25 × 1 cm column packed with Nucleosil 10 C 18 from Macherey-Nagle, eluted with 1 : 1 acetonitrile–water with 1% acetic acid) equipped with a printer–plotter–integrator Waters



R = H, Br, or OCH_3

Table 1. Results of direct photolysis of (1) (λ >360 nm)

Substituent R	Absorption maxima of (1) (nm) (ε/ l mol^{-1} cm^{-1})	Quantum yield at 405 nm [a]	Yield (%) [b] (2)	(3)
H	235 (7 780) 265 (9 920) 370 (3 510)	0.175 ± 0.025	20 ± 2	80 ± 2
Br	330 (9 030) 268 (11 940) 370 (3 980)	0.065 ± 0.005	10 ± 2	80 ± 2
OCH_3	235 (12 680) 270 (13 010)	0.06 ± 0.01	20 ± 2	80 ± 2

[a] Performed at room temperature. [b] Performed at 0 °C.

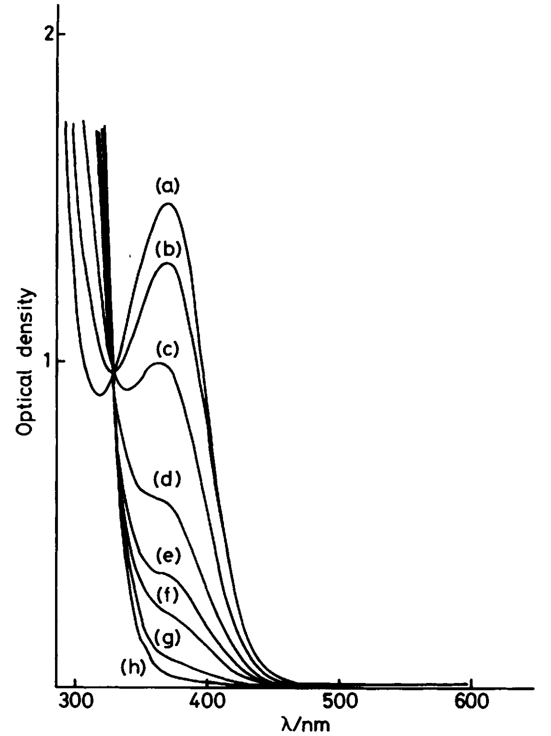
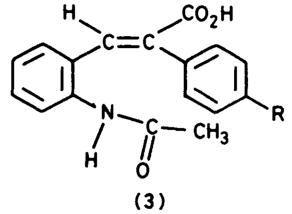
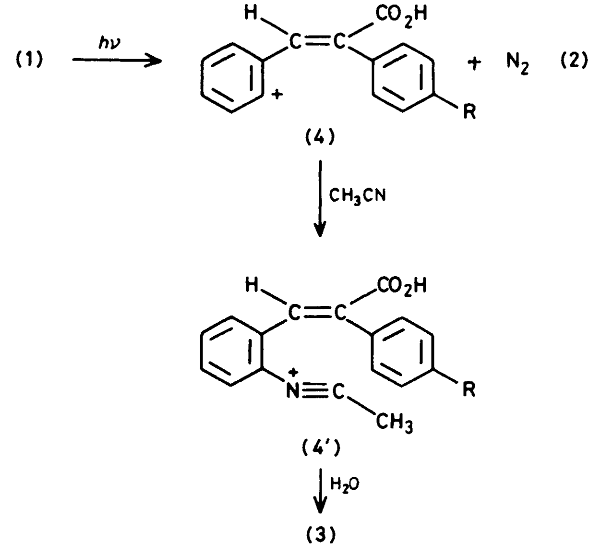


Figure 1. Spectral change evolution during irradiation with a 250 W Hg lamp at λ > 360 nm of (1; R = H) (4.2 × 10^{-3}M) in CH_3CN: (a) *t* 0; (b) *t* 2; (c) *t* 5; (d) *t* 10; (e) *t* 15; (f) *t* 21; (g) *t* 29; (h) *t* 41 min



(3)

R = H, Br, or CH_3



Associates data module. Assays were made using an external standard.

Photolysis Systems.—For the determination of quantum yields at 405 and 436 nm, the desired mercury emission line from a 250 W Hg lamp (Applied Photophysics type ME/D) was isolated by using band pass filters (Oriel models 5644 and and 5645). Light intensities absorbed by the samples were measured as reported previously.[17] Quantum yield determinations were done spectrophotometrically at the maximum wavelength of the absorption of (1) by comparing the absorption of the sample before and after irradiation.

The photolysis apparatus for preparative experiments consists of an Osram 250 W Xe lamp equipped with T_2 and Ta_2 M.T.O. filters to avoid i.r. light and Corning filters (3-73 or 3-75) to select the desired area of the visible spectra.[17] Typically an acetonitrile solution containing 5mM-(1) purged with dry argon was irradiated until the total disappearance of (1) (2.5 h) and then subjected to h.p.l.c. analysis. Throughout the irradiation the sample solution was thermostatted at 0 ± 2 °C by an ethanol stream through a glass jacket to prevent the slow thermal decomposition of (1). The same procedure was used to irradiate solutions of 4mM-(1) in the presence of a 20-fold deficit of $Ru(bpy)_3^{2+}$. Solutions were irradiated for 20 min.

Results and Discussion

Direct Photolysis of the Diazonium Salts (1).—All diazonium ions (1), as BF_4^- salts, studied here absorb light strongly in acetonitrile with two bands in the u.v. and a third, low-energy band, centred around 370—410 nm (Table 1). Direct irradiation (λ_{ex} > 360 nm) of (1) in deaerated acetonitrile in this absorption band induces the complete degradation of (1) as reflected by the evolution of the electronic absorption spectrum with time (Figure 1). The quantum yield of the transformation measured at 405 ± 4 nm is moderately low (Table 1) as is its rate constant. Analysis and isolation by h.p.l.c. of the final products after photolysis show that only a small amount of the corresponding phenanthrene (2) is formed (10—20%), while the main product of the reaction is the acetamide derivative (3) (see Table 1 for yields). The structure of (3) was assigned on the basis of spectral data and confirmed by comparison with an authentic sample prepared by a more conventional route.[12]

It has been demonstrated previously that direct photolysis of benzenediazonium salts leads to the corresponding aryl cation.[18] By assuming the same primary photolytic process [equation (2)] the appearance of (3) probably results from the addition of acetonitrile to the corresponding aryl cation (4)

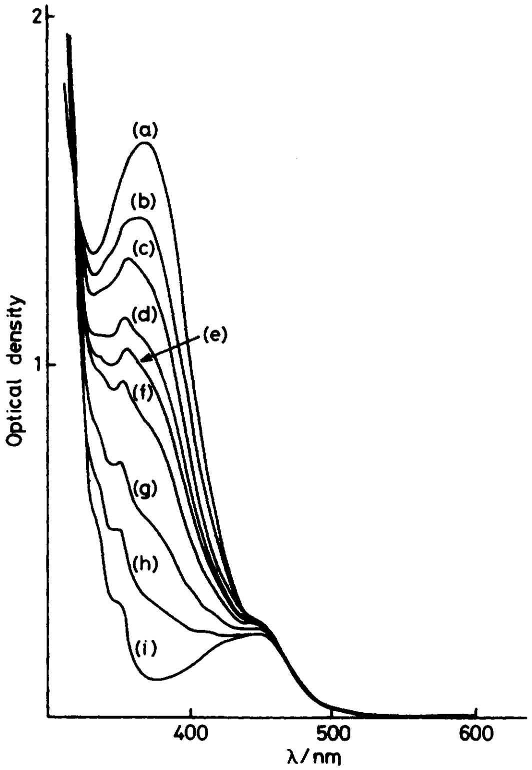


Figure 2. Spectral change evolution during irradiation with a 250 W Hg lamp at λ > 400 nm of $Ru(bpy)_3^{2+}$ (1.8×10^{-4}M) with (1; R = H) (4.3×10^{-3}M) in CH_3CN: (a) *t* 0; (b) *t* 10 s; (c) *t* 21 s; (d) *t* 32 s; (e) *t* 42 s; (f) *t* 1 min 3 s; (g) *t* 1 min 34 s; (h) *t* 2 min 20 s; (i) *t* 7 min 37 s

followed by hydrolysis of the resulting aryl cation adduct (4′). The hydrolysis takes place at the h.p.l.c. analysis stage (see Experimental section). The same reactivity of cations toward acetonitrile and water has been observed for benzyl cations obtained by electrochemical oxidation in a polymethylbenzene series.[19] The small amount of phenanthrene (2) comes most likely from cyclization of the aryl free radical (5) which be should concurrently formed with the aryl cation (4) during photolysis rather than from the cyclization of (4).

These results show clearly that the Pschorr reaction does not occur with high efficiency by direct irradiation of (1) in acetonitrile.†

Photolysis of (1) *in the Presence of* $Ru(bpy)_3^{2+}$.—Selective irradiation (λ_{ex} >410 nm) of $Ru(bpy)_3^{2+}$ in *ca.* 20-fold deficit over (1) in argon-purged acetonitrile induces rapid disappearance of (1) as illustrated by the evolution of the electronic absorption spectra (Figure 2). The last spectrum indicates that $Ru(bpy)_3^{2+}$ is not consumed after the complete transformation of (1). Contrary to observations for direct photolysis, the phenanthrene derivative (2) is obtained in 100% yield, for R = H, Br, and OCH_3, as demonstrated by h.p.l.c. assay and by isolation of the final product. Table 2 gives the quantum yields which are markedly larger than for the direct photolysis. Our data suggest that electronic effects by substituent groups R do not play a major role.

Table 2. Photocatalysis of (1) by $Ru(bpy)_3^{2+}$ (λ >410 nm)

Substituent R	Quantum yield at 436 nm [a]	10^{-9} Quenching rate/k_q l mol^{-1} s^{-1} [a,b]
H	0.46	3.5
Br	0.78	5.5
OCH_3	0.60	3.8

[a] Performed at room temperature. [b] In 10^{-1}M-Bu_4NClO_4–CH_3CN solution.

Quenching Rate of Luminescence of $Ru(bpy)_3^{2+}$ *by* (1).—We have verified that (1) efficiently quenches the excited state of $Ru(bpy)_3^{2+}$. Luminescence intensity measurements give linear Stern–Volmer plots, which implies that the quenching is a simple bimolecular reaction. The quenching rate constants k_q were calculated from the Stern–Volmer plots and they are seen to approach the diffusion-controlled limit (Table 2). The facile, irreversible reduction of (1) ($E_{\frac{1}{2}}$ *ca.* −0.1 V in CH_3CN) which was demonstrated previously,[8] implies that oxidative quenching of the excited state $Ru(bpy)_3^{2+*}$ $\{E°[Ru(bpy)_3^{3+/2+*}]$ −0.8 V$\}$ [1] by electron transfer is spontaneous. However, energy transfer must also be taken into account as (1) has an absorption band close to the absorption band of $Ru(bpy)_3^{2+}$ ($\lambda_{max.}$ 454 nm in acetonitrile) and the possible triplet ‡ of (1) could be lower in energy than the lowest energy level of $Ru(bpy)_3^{2+*}$. Therefore, *a priori*, the quenching of $Ru(bpy)_3^{2+*}$ by (1) by energy transfer as observed for example with the anthracene-9-carboxylate anion,[21] cannot be rejected. However, the following experiment shows that electron transfer is probably the major pathway for quenching.

Conventional Microsecond Flash Photolysis Experiments.—Conventional flash photolysis with visible light (λ > 400 nm) of an oxygen-free solution of (1) where R = H (6×10^{-4}M) and $Ru(bpy)_3^{2+}$ (*ca.* 10^{-5}M) in acetonitrile shows the bleaching recovery of $Ru(bpy)_3^{2+}$ at 460 nm after the flash. Decay of that bleaching is significantly slower than that of a reversible back-electron-transfer following oxidative quenching[22] of $Ru(bpy)_3^{2+*}$. Total recovery of the initial signal is achieved in about a second. The weakness of the optical density change did not allow us to determine an accurate reaction order. No change in optical density is detected at 400, 550, and 600 nm. Taking into account the high quenching rate constant (k_q 3.5 × 10^9 l mol^{-1} s^{-1}) the observation of a slow recovery of $Ru(bpy)_3^{2+}$ following the flash is inconsistent with an energy-transfer mechanism. Thus $Ru(bpy)_3^{2+*}$ is probably quenched by electron transfer leading to $Ru(bpy)_3^{3+}$. The latter is slowly reduced to $Ru(bpy)_3^{2+}$ by an oxidizable long lived species produced during the reduction of (1).

Proposed Mechanism of Reaction.—According to the experimental observations given in the two preceding sections, the mechanism in the Scheme for the photochemical production of phenanthrene is reasonable. Equations (3)—(5) summarize the mechanism of formation by electron-transfer quenching of the free aryl radical (5) which is the key transitory species in the photocatalytic production of phenanthrene (2). Questions remain as to how the cyclization and subsequent reduction of $Ru(bpy)_3^{3+}$ occur. We suggest that the cyclization occurs by a radical pathway [equation (6)] followed by oxidation by $Ru(bpy)_3^{3+}$ of the cyclized radical which leads to the cation

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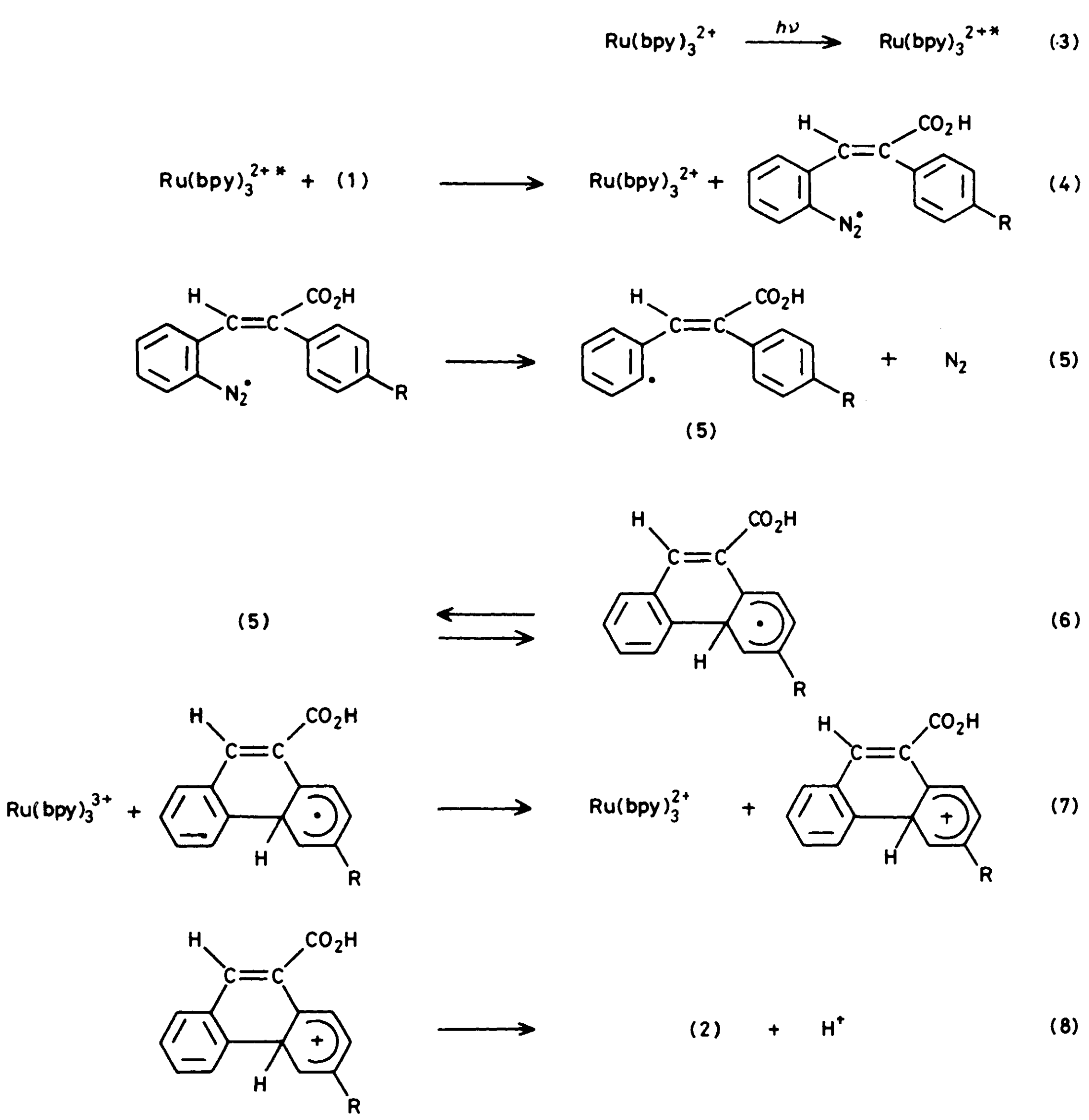
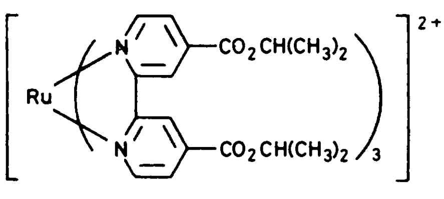
† Photoinduced Pschorr reaction by direct photolysis of a diazonium salt is very seldom observed.[20] The reaction occurs in acidic aqueous solution with a moderate yield.

‡ Irradiation into the absorption band (370—410 nm) of (1) does not result in any emission at room temperature. No attempt was made to obtain a phosphorescence spectrum at lower temperature.



Scheme.

[equation (7)]. The latter would give phenanthrene by loss of a proton. Electrochemical analysis of the final solution shows that one proton per mole of (1) is produced after photolysis. It may be conceivable that phenanthrene arises from direct oxidation by Ru(bpy)$_3^{3+}$ of the free radical (5) to give the cation (4) which cyclizes to (2). However, this mechanism is improbable because no acetamide derivative (3) was detected at the end of the photolysis.



(6)

Quenching of Other Polypyridyl Complexes of Ruthenium(II) *by* (1).—In order to test the hypothesis that the quenching of Ru(bpy)$_3^{2+*}$ by (1) occurs by electron transfer, we have also studied the ligand-modified complex (6). In complex (6) the formal electrochemical potential is more anodic [14] by *ca.* 0.4 V making it less easy to oxidize than Ru(bpy)$_3^{2+}$ while its excited-state energy is only slightly lower than that of Ru(bpy)$_3^{2+*}$. Consequently, it is not surprising to observe that (1; R = H) quenches the luminescence of (6) at a lower rate (k_q 0.42 × 10^9 l mol^{-1} s^{-1}) than for Ru(bpy)$_3^{2+}$ (k_q 3.5 × 10^9 l mol^{-1} s^{-1}) and that the quantum yield of disappearance of (1) at 436 nm is lower (φ 0.32 against 0.46). The less rapid rate of quenching of the excited state of (6) is consistent with a less favourable free-energy change if it is assumed that quenching operates by an electron-transfer process. However, some care must be taken in this statement since it has been claimed [14] that in comparing the quenching of (6)* and Ru(bpy)$_3^{2+*}$ by positively charged electron acceptors, the lower rate constant observed toward the quenching of Ru(bpy)$_3^{2+*}$ could be due, in part, to the shielding effect of the modified ligand.

Net Photo-oxidation of Ru(bpy)$_3^{2+}$ *by* 4-*Bromobenzenediazonium Salt*.—Another indirect proof of the electron-

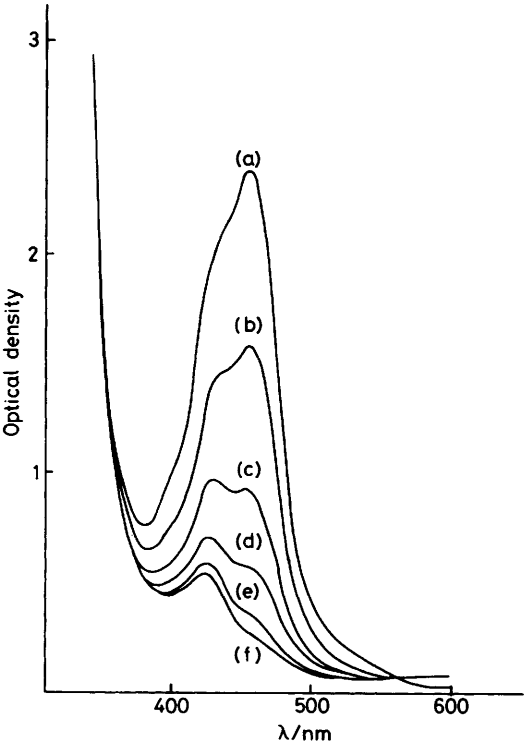


Figure 3. Spectral change evolution during irradiation with a 250 W Hg lamp at λ > 400 nm of $\mathrm{Ru(bpy)_3^{2+}}$ (1.7×10^{-4}M) with 4-Br-$\mathrm{C_6H_4N_2^+}$ $\mathrm{BF_4^-}$ (10^{-2}M) in $\mathrm{CH_3CN}$: (a) *t* 0; (b) *t* 11 s; (c) *t* 22 s; (d) *t* 34 s; (e) *t* 44 s; (f) *t* 55 s

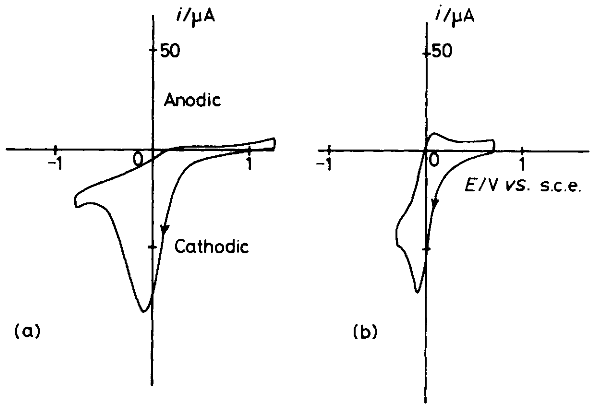


Figure 4. Cyclic voltammograms of: (a) 2×10^{-3}M-4-$\mathrm{BrC_6H_4N_2^+}$ $\mathrm{BF^{4-}}$ in 10^{-1}M-$\mathrm{Bu_4NClO_4}$–$\mathrm{CH_3CN}$ solution; (b) 2×10^{-3}M (1; R = H) in 10^{-1}M-$\mathrm{Bu_4NClO_4}$–$\mathrm{CH_3CN}$ solution. Pt electrode area 19.6 mm^2, sweep rate 0.1 V s^{-1}

transfer quenching mechanism can be obtained by using a simpler salt such as 4-bromobenzenediazonium ($\mathrm{BrC_6H_4N_2^+}$). This type of diazonium ion is known to be easily reducible[23] and to act as a quencher of triplet photosensitizers *via* electron-transfer quenching.[24] Irradiation of the 4-bromobenzenediazonium cation as the $\mathrm{BF_4^-}$ salt in oxygen-free acetonitrile leads to the net photogeneration of $\mathrm{Ru(bpy)_3^{3+}}$. Figure 3 shows the evolution of the spectral changes during the photolysis. The final spectrum is identical with that[25] of $\mathrm{Ru(bpy)_3^{3+}}$. Permanent build-up of $\mathrm{Ru(bpy)_3^{3+}}$ arises by electron-transfer quenching [equations (9) and (10)]. The back

$$\mathrm{Ru(bpy)_3^{2+}} \xrightarrow{h\nu} \mathrm{Ru(bpy)_3^{2+*}} \qquad (9)$$

$$\mathrm{Ru(bpy)_3^{2+*}} + \mathrm{BrC_6H_4N_2^+} \longrightarrow \mathrm{Ru(bpy)_3^{3+}} + \mathrm{BrC_6H_4N_2^{\cdot}} \qquad (10)$$

electron-transfer reaction is suppressed by the fast, irreversible reactions of $\mathrm{BrC_6H_4N_2^{\cdot}}$ [equations (11) and (12)]. The

$$\mathrm{BrC_6H_4N_2^{\cdot}} \longrightarrow \mathrm{BrPh^{\cdot}} + \mathrm{N_2} \qquad (11)$$

$$\mathrm{BrPh^{\cdot}} \longrightarrow \text{products} \qquad (12)$$

final products from the evolution of BrPh$^{\cdot}$ are still unknown.[26] The difference between the reactivity towards $\mathrm{Ru(bpy)_3^{2+*}}$ of the diazonium salts (1) and of 4-bromobenzene has its origin in the difference in rates of the subsequent reactions of their respective free radicals (5) (or its cyclized form) and Br-Ph$^{\cdot}$. The radicals are the results of electron-transfer quenching and dediazotization. Cyclic voltammetric observations perfectly illustrate this difference (see Figure 4). The reduction of $\mathrm{BrC_6H_4N_2^+}$ is totally irreversible while the reduction of (1) is partially reversible (E_{pa}/E_{pc} 0.5 at 0.1 V s^{-1}; ΔE_p *ca.* 0.2 V). It appears from the reverse scan of the voltammogram that reduction of (1) generates a species, the free radical (5), or more probably its cyclized form [equation (6)] (E_{pa} *ca.* 0.1 V) which can be easily oxidized by $\mathrm{Ru(bpy)_3^{3+}}$ {$E°[\mathrm{Ru(bpy)_3^{3+/2+}}]$ 1.3 V}. In the proposed mechanism, the oxidation by $\mathrm{Ru(bpy)_3^{3+}}$ [equation (3)] appears to be a slow process, as it is shown from the flash photolysis experiments, probably because of a slow cyclization step [equation (6)]. Free radical (5) could not be oxidized by $\mathrm{Ru(bpy)_3^{3+}}$. In the case of $\mathrm{BrC_6H_4N_2^+}$ the free radical BrPh$^{\cdot}$ reacts very rapidly, in particular with the solvent,† before electron transfer to $\mathrm{Ru(bpy)_3^{3+}}$ can occur.

Attempts are currently being made to apply this original Pschorr synthesis to related Pschorr-type reactions for which the yields are usually low using the more conventional procedures.

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† It has been shown that the phenyl radical arising from the electrochemical reduction of benzenediazonium salts in acetonitrile can be trapped by solvent or by aromatic compounds such as benzene or pyridine.[27]

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