

## A Photocatalytic Acid- and Base-Free Meerwein–Ponndorf–Verley-Type Reduction Using a $[\text{Ru}(\text{bpy})_3]^{2+}$ /Viologen Couple

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**Abstract:** A photocatalytic system to effect the Meerwein–Ponndorf–Verley reduction of carbonylic compounds to alcohols has been developed. The system comprises  $[\text{Ru}(\text{bpy})_3]^{2+}$  as a photosensitizer, triethanolamine as a sacrificial electron donor, viologen as an electron acceptor, and the carbonyl compound and *i*PrOH as Meerwein–

Ponndorf–Verley reagents. The photocatalytic reaction can be performed in neat *i*PrOH or in 1-butyl-3-methylimi-

dazolium ionic liquid. Mass spectrometric detection of the viologen hydride derivative  $\text{VH}^+$  confirms that this species is the reducing agent responsible for the carbonyl compound reduction. The reaction intermediates involved in the photocatalytic system have also been characterized by laser flash photolysis.

**Keywords:** ionic liquids · Meerwein–Ponndorf–Verley reduction · NADH · photocatalysis · ruthenium

### Introduction

Photocatalysis has focused predominantly on the degradation of organic pollutants in gaseous and aqueous media.<sup>[1]</sup> In contrast to the large number of publications dealing with the photocatalytic decomposition of organic compounds,<sup>[2]</sup> the number of examples reporting the use of photocatalysis to synthesize a desirable product (positive photocatalysis)<sup>[3–7]</sup> is considerably more scarce. Photocatalysis applied to chemical reactions may have an advantage over conventional thermal catalysis as photocatalysis can be performed at room temperature and avoids the use of acids, bases, and other noxious reagents. In the present work we report the selective photocatalytic reduction of carbonyl groups (Meerwein–Ponndorf–Verley-type reaction)<sup>[8]</sup> in *i*PrOH under neutral conditions by using  $[\text{Ru}(\text{bpy})_3]^{2+}$  as photocatalyst, viologens ( $\text{V}^{2+}$ ) as electron relays, and triethanolamine (TEOA) as a sacrificial electron donor.

As an alternative to the use of *i*PrOH as the solvent, we have performed the photocatalytic reaction in imidazolium ionic liquid. In this case, no  $\text{V}^{2+}$  is needed and the ionic liquid itself acts as electron relay and solvent. Ionic liquids are a very promising media for catalytic reactions.<sup>[9,10]</sup> Frequently the reaction products can be separated from the ionic liquid, while the catalyst remains in the ionic liquid and can be recovered and reused in many cycles.<sup>[9]</sup> Compared to reports of homogeneous catalysis, the use of ionic liquids as media for photochemical reactions remains almost unexplored.<sup>[11–14]</sup> In conventional catalysis using ionic liquids in combination with transition metal catalysts, the ionic liquid generally plays a passive role, just providing a liquid medium with certain miscibility and polarity properties. In contrast, in our case the imidazolium ionic liquid plays an active role, transferring electrons from  $[\text{Ru}(\text{bpy})_3]^{2+}$  to the ketone.

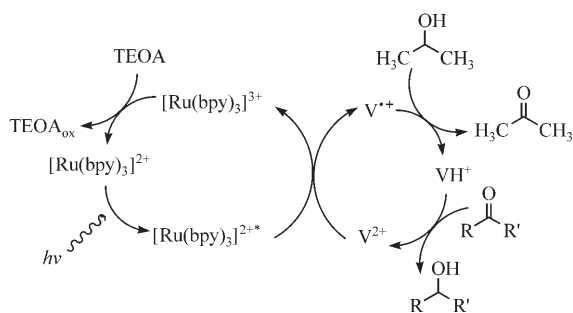
It is obvious that the unique properties of ionic liquids in terms of polarity, electron acceptor ability, limited diffusion, transparency, etc. can also be very useful to control the selectivity of photochemical reactions. Actually, photochemistry is always exploring new solvents and media to overcome the limited selectivity frequently exhibited by electronic excited states. Thus, on one hand, our report develops a novel photocatalytic process and on the other hand we provide an example to illustrate the potential of ionic liquids in photochemistry.

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## Results and Discussion

It is well known in photochemistry that  $[\text{Ru}(\text{bpy})_3]^{2+}$  triplet excited states are quenched by viologens through an electron-transfer mechanism giving rise to  $[\text{Ru}(\text{bpy})_3]^{3+}$  and viologen radical cation ( $\text{V}^{\bullet+}$ ).<sup>[15–17]</sup> The quenching rate constant depends on the redox potential of the viologen used, but for many cases the quenching occurs near diffusion control. Given the structure and radical nature of the viologen radical cation formed in the quenching, we anticipated that in the presence of good hydrogen atom donors, such as *i*PrOH, this viologen radical cation would abstract one hydrogen atom from the medium to form the corresponding 1-methyl-4-(1,4-dihydro-1-methylpyridinyl)pyridinium ( $\text{VH}^+$ ). This dihydro derivative  $\text{VH}^+$  is analogous to Meisenheimer complexes and NADH coenzyme and in a similar manner to these analogues, which function in many biological systems as reducing agents of carbonyl groups, it will tend to reform  $\text{V}^{2+}$  regaining aromaticity by transferring a hydride to an acceptor, such as a carbonyl compound, and will be ready to perform another catalytic cycle. The cycle is completed when  $[\text{Ru}(\text{bpy})_3]^{3+}$  abstracts one electron from TEOA, the sacrificial electron donor present in the medium to reform  $[\text{Ru}(\text{bpy})_3]^{2+}$ . This catalytic cycle is depicted in Scheme 1.



Scheme 1. Photocatalytic cycle to effect the Meerwein–Ponndorf–Verley reduction of a carbonyl group by *i*PrOH.

In agreement with our proposal (Scheme 1), in a preparative experiment mandelic acid is formed with almost complete selectivity (>95%) at high conversions (82%) by reduction of 2-phenyl-2-oxoethanoic acid upon illumination of an *i*PrOH solution of  $[\text{Ru}(\text{bpy})_3]^{2+}$ ,  $\text{V}^{2+}$ , and TEOA. The whole process corresponds to the Meerwein–Ponndorf–Verley reduction of 2-phenyl-2-oxoethanoic acid by *i*PrOH, promoted by illumination of the  $[\text{Ru}(\text{bpy})_3]^{2+}/\text{V}^{2+}$  couple in the presence of TEOA.

Control experiments in the absence of any of the four components (TEOA,  $[\text{Ru}(\text{bpy})_3]^{2+}$ ,  $\text{V}^{2+}$ , and 2-propanol) made the reduction of 2-phenyl-2-oxoethanoic acid stop, and the formation of the corresponding mandelic acid derived from the ketone reduction was not detected. Also a blank control in which all the components were present but the system was stored in the dark showed no conversion to the

product. The cycle is catalytic with respect to  $[\text{Ru}(\text{bpy})_3]^{2+}$  and  $\text{V}^{2+}$  as the photocatalyst and viologen are in a molar ratio of 0.16 and 0.06%, respectively, with respect to the substrate, while the number of moles of the ketone converted was much higher than the moles of  $[\text{Ru}(\text{bpy})_3]^{2+}$  or  $\text{V}^{2+}$  present, giving a turnover numbers of 600 and 1500 for  $[\text{Ru}(\text{bpy})_3]^{2+}$  and  $\text{V}^{2+}$ , respectively.

To show the generality of this photocatalytic Meerwein–Ponndorf–Verley reduction of carbonyl groups, two more carbonyl compounds, namely acetophenone and cyclohexanone, were also tested under the same photocatalytic conditions, whereby the corresponding alcohols were formed with chemical yields of 80 and 78%, respectively.

To provide evidence in support of the feasibility of some of the necessary steps in the mechanism illustrated in Scheme 1, the reaction was carried out in the absence of any ketone. Under these conditions, the irradiated solution became green and the transformation of viologen  $\text{V}^{2+}$  into its hydride derivative  $\text{VH}^+$  occurred as determined by reverse-phase HPLC–MS in which the disappearance of the peak at  $m/z = 93$  Da (mass of  $\text{V}^{2+}$  divided by 2) was accompanied by an increase of the peak at  $m/z = 187$  Da, corresponding to the expected hydride  $\text{VH}^+$ . Furthermore, rather unexpectedly a stationary (low but detectable) concentration of a peak at  $m/z = 186$  Da, attributable to the  $\text{V}^{\bullet+}$  radical cation was also observed. Observation of  $\text{V}^{\bullet+}$  in HPLC–ESI–MS can be rationalized when the fact that it is among the longest-lived radical cations is considered. In the absence of oxygen it has been found to be persistent enough to be characterized by conventional steady-state spectroscopic techniques, mainly optical spectroscopy.<sup>[18]</sup> Even in the presence of oxygen,  $\text{V}^{\bullet+}$  can be visually detected. Moreover, when the hydride derivative  $\text{VH}^+$  was alternatively prepared in high concentrations by  $\text{NaBH}_4$  reduction of the viologen, a species with the same mass spectrum and chromatographic retention time as that generated photochemically from the photocatalytic reduction by using  $[\text{Ru}(\text{bpy})_3]^{2+}$  and *i*PrOH was obtained. This provides firm support that quenching of  $[\text{Ru}(\text{bpy})_3]^{2+}$  excited triplets by  $\text{V}^{2+}$  in *i*PrOH forms the corresponding  $\text{VH}^+$  reducing agent. The use of 3-methyl-1-butanol as a solvent instead of *i*PrOH was also equally suited to form  $\text{VH}^+$ , but in this case, given its higher molecular mass, we had the chance to identify 3-methylbutanal, thus demonstrating that primary as well as secondary alcohols can serve as hydrogen atoms donors.

In contrast, when the photocatalytic reaction of  $[\text{Ru}(\text{bpy})_3]^{2+}$  and  $\text{V}^{2+}$  was attempted in the absence of alcohols or hydrogen donor solvents, the appearance of the  $\text{VH}^+$  product, corresponding to the abstraction of  $\text{H}^{\bullet}$  from the solvent by  $\text{V}^{\bullet+}$ , was not observed and the solution became deep blue under an Ar atmosphere, indicating the accumulation of the  $\text{V}^{\bullet+}$  radical cation. UV–Vis spectroscopy of the blue solution exhibited a band at  $\lambda_{\text{max}} = 600$  nm with fine structure corresponding to  $\text{V}^{\bullet+}$ . Upon admission of air, the blue color faded in agreement with the known reactivity of  $\text{V}^{\bullet+}$  with oxygen. If to this blue solution, 2,6-diphenylphenol is added then the blue color changes to green and MS analy-

sis again reveals the presence of  $\text{VH}^+$  ( $m/z = 187$  Da), generated by  $\text{H}^\bullet$  atom abstraction by the viologen radical cation from 2,6-diphenylphenol. This experimental data strongly supports the transformation of  $\text{V}^{2+}$  into  $\text{VH}^+$  in the presence of good hydrogen atom donors.

Concerning the quenching of  $[\text{Ru}(\text{bpy})_3]^{2+}$  triplet excited state by viologens, it is well known that the quenching rate constant increases with the reduction potential of the viologen until it becomes a diffusion control process. Thus, if instead of 4,4'- other bipyridiniums with 2,2'-substitution exhibiting different reduction potentials are used, the initial reaction rate of methyl mandelate formation ( $r_0$ ), measured as the slope at zero time of conversion versus time plot, correlates very well with the reported redox potentials,<sup>[19]</sup> thus suggesting that the quenching of the  $[\text{Ru}(\text{bpy})_3]^{2+}$  triplet excited state by  $\text{V}^{2+}$  plays an important role in controlling the overall rate of the photocatalytic cycle. Figure 1 provides a graphical representation of the correlation between the reduction potentials and  $r_0$  for the series of three viologens tested in this study.

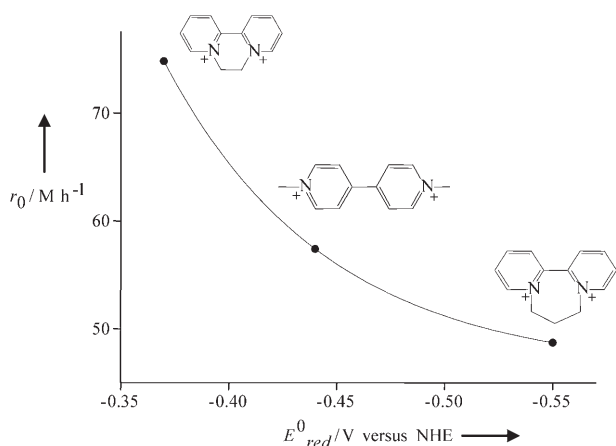
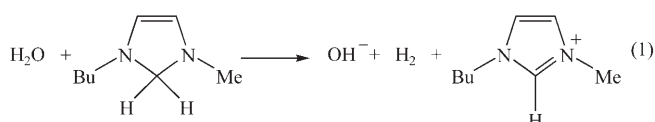


Figure 1. Initial reaction rates ( $r_0$ ) for the formation of methyl mandelate during the photocatalytic reduction as a function of the bipyridinium electron acceptor.

In view of the structural similarity between  $\text{V}^{2+}$  and 1-butyl-3-methylimidazolium ( $\text{bmim}^+$ ) we assumed that  $\text{bmim}^+$  can also form the hydride intermediate upon irradiation of  $[\text{Ru}(\text{bpy})_3]^{2+}$  in the presence of a good hydrogen donor. In fact, if the imidazolium ionic liquid medium containing  $[\text{Ru}(\text{bpy})_3]^{2+}$  and  $i\text{PrOH}$  ( $\text{bmim-BF}_4/i\text{PrOH}$  weight ratio 5) is irradiated with visible light, the corresponding mandelate is generated when methyl benzoylformate ketone is added. For making the process fully photocatalytic, the concentration of  $[\text{Ru}(\text{bpy})_3]^{2+}$  was reduced up to a substrate-to-photocatalyst ratio of 500 and TEOA was added as the sacrificial electron donor regenerating  $[\text{Ru}(\text{bpy})_3]^{2+}$  from  $[\text{Ru}(\text{bpy})_3]^{3+}$ . The actual photocatalytic cycle is identical to that presented in Scheme 1 with the viologen species replaced by the imidazolium cations.

To demonstrate the versatility of the hydride adduct of  $\text{bmim}^+$  to perform other photocatalytic reactions that differ from carbonyl reductions, we added a proton donor to the  $\text{TEOA}/[\text{Ru}(\text{bpy})_3]^{2+}/\text{bmim-BF}_4$  photocatalytic system, namely water. According to the chemical behavior of a Meisenheimer complex, we anticipated that if instead of a carbonyl compound water is present in the medium, then the intermediate hydroimidazole would decompose and hydrogen gas would be generated and observed visually. The process is described by Equation (1) and is analogous to the well-established  $\text{H}_2$  generation in the  $[\text{Ru}(\text{bpy})_3]^{2+}/\text{V}^{2+}$  couple.

The reaction mechanism proposed in Scheme 1 was validated by means of several control experiments. Thus, the in-



termediate H-imidazole was generated alternatively by reduction of an excess of 1-butyl-3-methylimidazolium with  $\text{LiAlH}_4$ . The reduction and the consequent generation of 1-butyl-3-methyl-2,2-dihydroimidazole was followed by  $^1\text{H}$  NMR spectroscopic analysis with a solution of  $\text{bmim-BF}_4$  in  $\text{CDCl}_3$ , whereby the disappearance of the signal at  $\delta = 9.5$  ppm corresponding to the H-2 proton of 1-butyl-3-methylimidazolium cation was accompanied by the appearance of the signal of the methylene group at the 2-position of the H-imidazole intermediate at  $\delta = 4.8$  ppm. At this point, the chemically generated H-imidazole intermediate was treated with methyl benzoylformate or with  $\text{D}_2\text{O}$ . In both cases, the signal corresponding to the methylene group of the intermediate H-imidazole at  $\delta = 4.8$  ppm disappears and the signal of the imidazolium cation at  $\delta = 9.5$  ppm reappears. This experiment clearly shows the feasibility of the part of the proposed mechanism in Scheme 1 concerning the reduction of a carbonyl group by H-imidazole and Equation (1) with respect to hydrogen generation.

To obtain spectroscopic evidence for the formation of the dihydro derivative  $\text{VH}^+$  in a photocatalytic system, such as indicated in Scheme 1, we performed laser flash photolysis measurements of the individual components of the system as well as of the whole photocatalytic system. The aim was to obtain evidence for the generation of a hydride donor species from a strong electron acceptor viologen in an ionic liquid, which is a suitable solvent for the process.

With this aim in mind, 532 nm laser excitation of the  $[\text{Ru}(\text{bpy})_3]^{2+}$  in ionic liquid  $\text{bmim-BF}_4$  allows the recording of a transient absorption spectrum attributable to the triplet excited state of this complex (Figure 2). The half life of the triplet excited state of  $[\text{Ru}(\text{bpy})_3]^{2+}$  in  $\text{bmim-BF}_4$ , obtained from the fit of the signal monitored at 350 nm, was estimated to be 960 ns (see inset of Figure 2). The  $[\text{Ru}(\text{bpy})_3]^{2+}$  triplet lifetime in  $\text{bmim-BF}_4$  is significantly longer than that

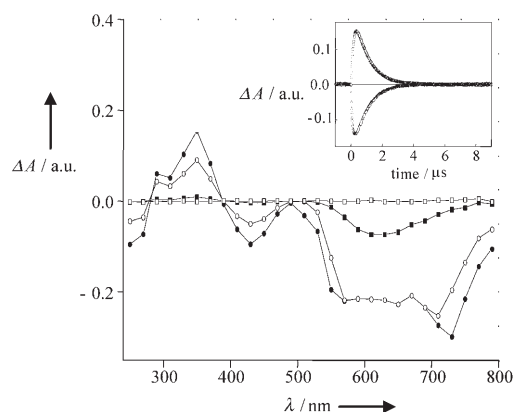


Figure 2. Transient absorption spectra of the  $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$  complex ( $1 \times 10^{-4} \text{ M}$ ) in  $\text{bmim-BF}_4$  recorded at 0.5 ( $\bullet$ ), 1 ( $\circ$ ), 3 ( $\blacksquare$ ), and 8 ( $\square$ )  $\mu\text{s}$  after 532 nm laser excitation. The inset shows the temporal profiles for the signals monitored at 350 ( $\circ$ ) and 420 nm ( $\Delta$ ).

recorded for the 680 ns half life same transient in acetonitrile. This longer triplet lifetime is, in principle, beneficial for promoting photochemical processes from this excited electronic state and may reflect the influence of the polarity of the medium on the metal-to-ligand charge transfer  $[\text{Ru}(\text{bpy})_3]^{2+}$  triplet excited state and/or its high viscosity, reducing the diffusion coefficient as compared to conventional organic solvents.

As expected, the addition of  $\text{MV}(\text{PF}_6)_2$  to a  $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$  solution in  $\text{bmim-BF}_4$  quenched the triplet excited state of the  $[\text{Ru}(\text{bpy})_3]^{2+}$  through a photoinduced electron-transfer process as evidenced by time-resolved spectroscopy. Figure 3 shows the transient absorption spectra recorded as long as 150  $\mu\text{s}$  after 532 nm laser excitation of the  $[\text{Ru}(\text{bpy})_3]^{2+}$  in  $\text{bmim-BF}_4$  in the absence and in the presence of  $10^{-2} \text{ M}$  concentration of  $\text{V}^{2+}$ . At this long delay time in the absence of  $\text{V}^{2+}$ , no bands for the triplet excited state of the  $[\text{Ru}(\text{bpy})_3]^{2+}$  complex were observed, indicating that the  $[\text{Ru}(\text{bpy})_3]^{2+}$  triplet decays completely in a much shorter timescale, as mentioned earlier. In contrast, in the presence of a  $10^{-2} \text{ M}$  concentration of  $\text{V}^{2+}$  the transient absorption spectrum shows two strong absorption bands at  $\lambda_{\text{max}} = 380$  (sharper) and 500–650 nm (broader, structured). These two

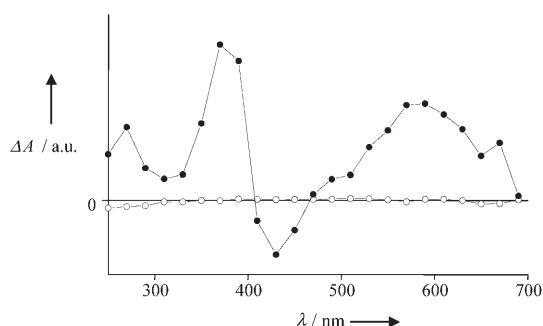


Figure 3. Transient absorption spectra of  $[\text{Ru}(\text{bpy})_3]^{2+}$  in  $\text{bmim-BF}_4$  in the absence ( $\circ$ ) and in the presence ( $\bullet$ ) of  $10^{-2} \text{ M}$  quencher  $\text{MV}(\text{PF}_6)_2$  recorded at 150  $\mu\text{s}$  after 532 nm laser excitation.

bands are the characteristic transient absorption spectrum of the viologen radical cation. Observation of the viologen radical cation absorption spectrum confirms the occurrence of photoinduced electron transfer from the  $[\text{Ru}(\text{bpy})_3]^{2+}$  triplet excited state to  $\text{V}^{2+}$ . The negative absorption band at  $\lambda_{\text{max}} = 430 \text{ nm}$  indicates that the  $[\text{Ru}(\text{bpy})_3]^{2+}$  ground state has not yet completely recovered at this time delay. Thus, although our transient spectrum does not show evidence for the presence of other species besides  $\text{V}^{+}$ , the bleaching of the  $[\text{Ru}(\text{bpy})_3]^{2+}$  ground state indicates indirectly that other Ru species must still be present. We speculate that this Ru species should be  $[\text{Ru}(\text{bpy})_3]^{3+}$  ( $\lambda_{\text{max}} = 360 \text{ nm}$ ), thus coinciding with the absorption bands assigned for  $\text{V}^{+}$ , the latter having larger extinction coefficients.

We commented above that in the preparative experiments the presence of  $\text{V}^{2+}$  is not absolutely necessary and that the imidazolium ionic liquid can also act as electron acceptor. Laser flash photolysis experiments, however, do not give any indication of the quenching of  $[\text{Ru}(\text{bpy})_3]^{2+}$  triplets by the ionic liquid. These two contradictory observations can be reconciled by assuming that the quenching rate constant of  $[\text{Ru}(\text{bpy})_3]^{2+}$  triplets by imidazolium is smaller than  $10^4 \text{ M}^{-1} \text{ s}^{-1}$ . It is known that nanosecond laser flash studies are able to provide kinetic information in the microsecond timescale, this means for those processes producing kinetic constants of about  $10^6 \text{ s}^{-1}$ , thus laser flash photolysis as a fast kinetic technique is not appropriate to measure slow processes taking place in timescales longer than hundreds of microseconds. Of course, this also means that the quenching of imidazolium will not be very efficient and that most of the  $[\text{Ru}(\text{bpy})_3]^{2+}$  triplets will decay to the ground state without undergoing electron transfer as it is observed in the transient spectra. This is in contrast with  $\text{V}^{2+}$ , which is able to quench most of the  $[\text{Ru}(\text{bpy})_3]^{2+}$  triplets.

After generation, the  $\text{V}^{+}$  radical cation is very long-lived in  $\text{bmim-BF}_4$  ionic liquid. Thus, the characteristic transient absorption spectrum of the  $\text{V}^{+}$  radical cation can be detected at times longer than 800  $\mu\text{s}$  after the laser pulse. Figure 4 shows the signals monitored at  $\lambda_{\text{max}} = 380$  and 600 nm at the longest timescale available to our ns laser flash set-up. The temporal profile of these two signals is very similar, particularly after the first 300  $\mu\text{s}$ , suggesting that at short timescales there may be a residual absorption due to a shorter-lived transient decaying in hundreds of  $\mu\text{s}$ , but after this interfer-

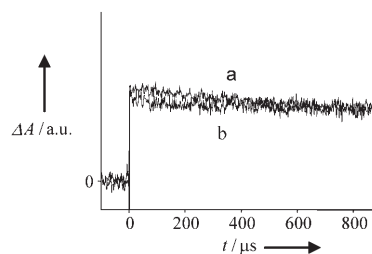
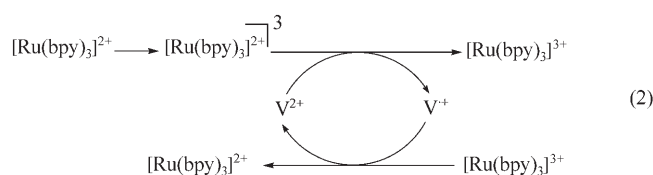


Figure 4. Transient signals after 532 nm excitation of the solution  $[\text{Ru}(\text{bpy})_3]^{2+}$  in  $\text{bmim-BF}_4$  in the presence of  $10^{-2} \text{ M}$   $\text{MV}(\text{PF}_6)_2$  monitored at 380 nm (a) and 600 nm (b) in a long timescale.

ence they correspond to the same species, that is, the viologen radical cation. The decay kinetics of the signal at 600 nm fits well with second-order kinetics with a  $k=3.6 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ . This fit to second-order kinetics is also compatible with the back electron-transfer process between the viologen radical cation and the  $[\text{Ru}(\text{bpy})_3]^{3+}$  as the predominant disappearance process. From the relative intensity of the bleaching at  $\lambda_{\text{max}}=430 \text{ nm}$ , absorption at  $\lambda_{\text{max}}=380 \text{ nm}$ , and their corresponding extinction coefficients, it can be deduced that the molar ratio between  $\text{V}^{2+}$  and bleached  $[\text{Ru}(\text{bpy})_3]^{2+}$  is 1:1. These data are consistent with Equation (2), describing the forward electron-transfer quenching of excited  $[\text{Ru}(\text{bpy})_3]^{2+}$  and the annihilation through back electron transfer.

Once we had studied the photochemical behavior of the couple  $[\text{Ru}(\text{bpy})_3]^{2+}/\text{V}^{2+}$  in  $\text{bmim-BF}_4$  ionic liquid, we pro-



ceeded to establish the influence of the presence of *i*PrOH on the evolution of the transients. According to Scheme 1, we expected that *i*PrOH could act as an efficient hydrogen donor for  $\text{V}^{\cdot+}$ . To obtain spectroscopic evidence for the feasibility of this hydrogen transfer, we submitted a solution of  $[\text{Ru}(\text{bpy})_3]^{2+}$  in  $\text{bmim-BF}_4/i\text{PrOH}$  containing  $\text{V}^{2+}$  as quencher to laser flash photolysis. In agreement with our speculation, Figure 5 shows that the presence of *i*PrOH produces spectral changes. Specifically, the band of  $\text{V}^{\cdot+}$  between  $\lambda_{\text{max}}=500\text{--}700 \text{ nm}$  peaking at  $\lambda_{\text{max}}=590 \text{ nm}$  is replaced by a new absorption band between  $\lambda_{\text{max}}=450\text{--}550 \text{ nm}$  peaking at  $\lambda_{\text{max}}=500 \text{ nm}$ . We assigned the band at  $\lambda_{\text{max}}=500 \text{ nm}$  as due

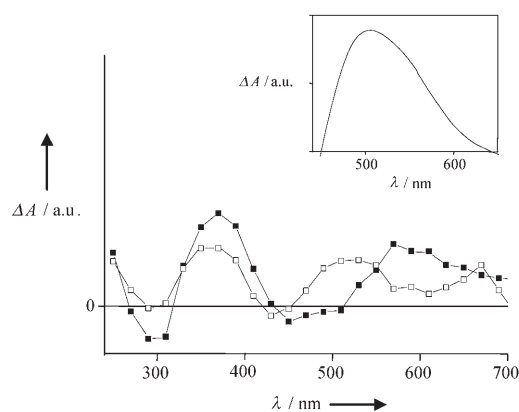


Figure 5. Transient absorption spectra recorded at 22  $\mu\text{s}$  after 532 nm laser excitation of the couple  $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2/\text{MV}(\text{PF}_6)_2$  in  $\text{bmim-BF}_4$  in the absence (■) and in the presence (□) of *i*PrOH (1:1 vol with respect to  $\text{bmim-BF}_4$ ). The inset shows the difference spectrum between that of a solution containing  $\text{V}^{2+}$  ( $9 \times 10^{-3} \text{ M}$ ) and  $\text{NaBH}_4$  ( $5 \times 10^{-3} \text{ M}$ ) in basic water and that of initial  $\text{V}^{2+}$ . The 500 nm band was assigned to the  $\text{VH}^+$  species.

to  $\text{VH}^+$  formed from  $\text{V}^{\cdot+}$  through hydrogen abstraction from *i*PrOH.

To provide some experimental evidence for the assignment of the  $\lambda_{\text{max}}=500 \text{ nm}$  visible band to  $\text{VH}^+$ , we proceeded to generate  $\text{VH}^+$  chemically by  $\text{NaBH}_4$  reduction of  $\text{V}^{2+}$  in acetonitrile, whereby a band at  $\lambda_{\text{max}}=500 \text{ nm}$  was recorded (see inset of Figure 5).

## Conclusion

In summary, by using the  $[\text{Ru}(\text{bpy})_3]^{2+}/\text{viologen}$  couple and TEOA as a sacrificial donor in a good hydrogen atom donor solvent, it has been possible to develop an efficient photocatalytic Meerwein–Ponndorf–Verley reduction in the absence of any strongly acidic or basic conditions that are usually required in conventional thermal catalysis. Our system is based on the conversion of viologen to dihydropyridine, the process resembling the natural  $\text{NADH}/\text{NAD}^+$  enzymatic factor of biological carbonyl reductions. The proposed mechanism for this photocatalytic system has been supported by using different steady-state spectroscopic techniques, such as MS,  $^1\text{H}$  NMR spectroscopy, and time-resolved laser flash photolysis.

## Experimental Section

All the chemicals used were commercial samples obtained from Aldrich and were used as received. Tetrafluoroborate of 1-butyl-3-methyl imidazolium,  $\text{bmim-BF}_4$ , is a commercial solvent from Solvent Innovation. Methyl viologen dichloride ( $\text{MVCl}_2$ ) and ruthenium tris-bipyridyl dichloride ( $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ ) were submitted to  $\text{Cl}^-/\text{PF}_6^-$  ion exchange by using a saturated aqueous solution of  $\text{NH}_4\text{PF}_6$ . In contrast to the initial chloride salts,  $\text{MV}(\text{PF}_6)_2$  and  $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$  were soluble in  $\text{MeCN}$  and  $\text{bmim-BF}_4$ . The  $\text{bmim-BF}_4$  solutions of  $\text{MV}(\text{PF}_6)_2$  and  $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$  were prepared by the addition of an appropriated volume of  $\text{MV}(\text{PF}_6)_2$  and  $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$  in acetonitrile to  $\text{bmim-BF}_4$ , mixing the liquids and exhaustive outgassing of the  $\text{bmim-BF}_4$  solution at  $50^\circ\text{C}$  under  $10^{-1}$  Torr to remove the acetonitrile.

Irradiation of the samples was carried out in a carousel by using a water refrigerated 125 W medium pressure mercury lamp through Pyrex. The samples (15 mL) were placed in test tubes capped with septa. Samples were purged with  $\text{N}_2$  at least 15 minutes before irradiation. The course of the reaction was followed by periodically analyzing aliquots, either through GC or HPLC analysis. For HPLC-MS, Agilent 1100 equipment was used. A reverse-phase C-18 column was employed by using  $\text{CF}_3\text{CO}_2\text{H}$  as an ionizing reagent and water-methanol as an eluent.

Photophysical measurements were carried out at room temperature. Laser flash photolysis experiments were carried out in a Luzchem ns laser flash system by using the second (532 nm, 50 mJ/pulse) harmonic of a Surelite Nd:YAG laser for excitation (pulse = 10 ns) and a 175 W ceramic Xenon Fiberoptic Lightsource, Cermax, perpendicular to the laser beam, as a probing light. The signal from the monochromator/photomultiplier detection system was captured by a Tektronix TDS 3032B digitizer. Laser system and digitizer were connected to a PC computer by GPIB and serial interfaces that controlled all the experimental parameters and provided suitable processing and data storage capabilities. The software package has been developed in the LabVIEW environment from National Instruments and compiled as a stand-alone application. Fundamentals<sup>[20]</sup> and details<sup>[21]</sup> of a similar time-resolved laser setup has been published elsewhere. The samples contained in a suprasil quartz



0.7×0.7 cuvette capped with septa were purged by N<sub>2</sub> flow at least 15 minutes before the laser experiments.

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