suggesting the existence of a series of competing processes.

Transient absorbance measurements[13] were conducted at room temperature in methylene chloride and the results of a typical experiment are shown in Figure 1 for both the model and the CQ complex. The difference spectrum for the model complex is characteristic of that expected for an MLCT based excited state with a strong increase in absorbance at $\lambda_{max} = 375$ nm due to the bipyridyl anion and a decrease in absorbance at $\lambda_{max} = 455$ nm arising from bleaching of the ground state $Ru^{II} \rightarrow$ bpy MLCT absorption band. For the CQ complex the difference spectrum is that expected for a charge-separated or interligand-charge-transfer (ILCT)[14] excited state with absorbance features appearing for the radical cations 10-MePTZ$^+$ ($\lambda_{max} = 516$ nm)[15] and Me(bpy)-3DQ$^+$ ($\lambda_{max} = 395$, 514 nm)[11b] and no bleaching at 455 nm. A calculated difference spectrum based on the known spectra of 10-MePTZ$^+$ and Me(bpy)-3DQ$^+$ is shown as an overlay in Figure 1.[16] That the site of reduction following excitation is DQ^{2+} and not bpy is supported by the red shift of ~20 nm in the feature at 395 nm and by the appearance of the feature at 515 nm which is a DQ$^+$-based absorption that overlaps with an absorption due to PTZ$^+$. The absence of bleaching at ~455 nm shows that the Ru^{II}–bpy chromophore is present in the charge-separated state. At room temperature in methylene chloride the ILCT state appears during the laser pulse (6 ns), suggesting that the intramolecular quenching events leading to the state are rapid ($k > 10^8$ s^{-1}). Once formed, the ILCT state decays via first-order kinetics with $k_{obsd} = 6.3 \times 10^6$ s^{-1}, independent of excitation intensity from 2 to 20 mJ/pulse. On the basis of the absorbance changes observed in the figure and using ϵ^* (375 nm) = 2.9×10^4 M^{-1} cm^{-1} for $Ru(bpy)_3^{2+*}$ [14] and ϵ(514 nm) = 4.4×10^3 M^{-1} cm^{-1} for Me(bpy)-3DQ$^+$,[11b] we estimate that the quantum yield of formation of the ILCT state is $\phi_{sep} = 0.26 \pm 0.04$.

Our observations and the known redox properties of related systems lead to the quenching scheme in Scheme I where the simplified abbreviations DQ^{2+}b and bPTZ have been adopted for the ligands Me(bpy)-3DQ^{2+} and Me(bpy)-PTZ. In this scheme MLCT sensitization of the ILCT state could occur by either of two branches depending on whether the initial quenching act is oxidative (k_2) or reductive (k'_2) in nature.

Although emission is observed at low temperature, by room temperature it is completely quenched, $k_2(k'_2) >> 1/\tau_{CT}(1/\tau'_{CT})$. The fact that $\phi_{sep} < 1.0$ suggests the importance of intramolecular recombination events like k_5 or k'_5. Factors that may contribute to the lifetime of the charge-separated ILCT state include a possible rate inhibition arising from the fact that both the reduced acceptor and oxidized donor site are positively charged and the fact that space-filling molecular models indicate that direct π overlap between the redox sites is possible.

From the potential differences between the $-PTZ^{+/0}$ and $-DQ^{2+/+}$ couples, it can be estimated that the energy of the ILCT state above the ground state is $\Delta G^{\circ\prime} \sim 1.29$ eV. The excited state is sufficiently long lived to carry out net redox chemistry. In the presence of 4.0×10^{-2} M Cu^{II} in acetonitrile, quenching of the ILCT state occurs via

$$PTZ^+–Ru^{II}–DQ^+ + Cu^{2+} \xrightarrow{\text{fast}} PTZ^+–Ru^{II}–DQ^{2+} + Cu^+ \quad (1)$$

and, as monitored by conventional flash photolysis,[17] the subsequent recombination reaction follows equal-concentration, second-order kinetics with $k_q = 4.3 \times 10^8$ M^{-1} s^{-1}:

$$PTZ^+–Ru^{II}–DQ^{2+} + Cu^+ \xrightarrow{k_q} PTZ–Ru^{II}–DQ^{2+} + Cu^{2+} \quad (2)$$

In the sequence of reactions, (1) followed by (2), the $Cu^{II/I}$ couple has been used to "discharge" the ILCT state by consecutive outer-sphere electron transfer steps. The experiment also serves to verify that MLCT excitation at room temperature does indeed lead to a PTZ$^+$ site since the difference spectrum after Cu^{II} quenching of the ILCT state (eq 1) shows only the band expected for PTZ$^+$ with absorption features for DQ$^+$ not present, as expected.

Our experiments demonstrate the existence of a MLCT-sensitized charge-separation process that yields separated redox equivalents and that the ILCT state reached can undergo chemical reactions. The charge storage time of $\tau_{sep} = 165 \pm 14$ ns is not overly long, but it may be possible to extend it considerably by eliminating the structural flexibility associated with the tetramethylene links to the phenothiazine group.

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Registry No. $[Ru(Me(bpy)\text{-}3DQ^{2+})(Me(bpy)\text{-}PTZ)_2]^{4+}$, 106763-61-5; $[Ru(Me(bpy)\text{-}PTZ)_2Cl_2]$, 106763-62-6; $[Me(bpy)\text{-}3DQ](PF_6)_2$, 96897-08-4.

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[13] Transient absorbance experiments were conducted with a Quanta-Ray DCR-2(20) Nd:YAG laser pumping Coumarin 460 dye in a Quanta-Ray PDL-1 dye laser producing an excitation pulse of 6 ns at 5 mJ/pulse. The probe beam, at right angle to the excitation beam, was provided by a pulsed Osram XBO 150-W xenon lamp. Electronic synchronization of the laser and probe was provided by electronics of our own design. The absorption signals were collected with quartz optics (*f*3.5) and imaged onto the slit of a 0.5 m (*f*3.4) monochromator and detected with a R446 5 stage PMT coupled to a Tektronix 7912AD transient digitizer interfaced to a DEC PDP-11/34 microcomputer.

[14] Truesdell, K. A.; Crosby, G. A. *J. Am. Chem. Soc.* **1985**, *107*, 1787.

[15] The absorbance maximum and extinction coefficient for 10-MePTZ$^{+\bullet}$ were determined by chemically oxidizing 10-MePTZ with Br_2. The 10-MePTZ was recrystallized twice and checked for purity by liquid chromatography. For the radical cation in CH_2Cl_2 in the visible region of the spectrum, $\lambda_{max} = 514 \pm 2$ nm, $\epsilon_{514} = 8050 \pm 72$ M^{-1} cm^{-1}.

[16] The calculated transient absorbance spectrum was obtained by superposition of the individual maxima for 10-MePTZ$^{\bullet+}$ and Me(bpy)-3DQ$^{\bullet+}$ having Lorenztian band shapes with their bandwidths adjusted, linearly in energy units, to agree with those observed spectroelectrochemically for the individual radical cations.

[17] (a) Details of the flash photolysis apparatus have been reported in ref 17b. Samples were freeze–pump–thaw degassed and appropriate filters employed to prevent irradiation higher in energy than 400 nm to prevent photoejection from PTZ. The apparatus was modified to provide optical triggering of the oscilloscope. (b) Young, R. C.; Keene, F. R.; Meyer, T. J. *J. Am. Chem. Soc.* **1977**, *99*, 2468.

[18] Chambron, J. C.; Sauvage, J. P. *Nouv. J. Chim.* **1985**, *9*, 527.

The Unusual Deacylation of the 2-Acetyl-1,3-dimethylbenzimidazolium Cation

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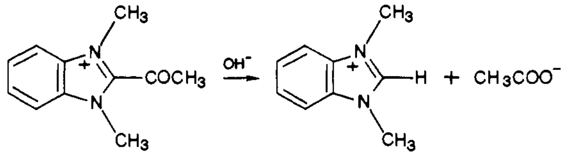
We report the unusual deacylation of the 2-acetyl-1,3-dimethylbenzimidazolium cation in aqueous solution. The cation is deacylated very rapidly by hydroxide ion even at pH 7–8, yet does not react with primary amines unless water is absent.



In the course of studies designed to prepare ketimines derived from the condensation of primary aliphatic and aromatic amines with 2-acylbenzimidazoles and perhaps to demonstrate a facilitated decarboxylation of α-amino acids in the presence of these ketones,[1] we had occasion to mix solutions of benzylamine and aniline in

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[1] Owen, T. C.; Young, P. R., Jr. *FEBS Lett.* **1974**, *43*, 308. Young, P. R., Jr.; Howell, L. G.; Owen, T. C. *J. Am. Chem. Soc.* **1975**, *97*, 6544. Lopatin, W.; Young, P. R. Jr.; Owen, T. C. *J. Am. Chem. Soc.* **1979**, *101*, 960.

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pyridine with solutions of 2-acetyl-1,3-dimethylbenzimidazolium chloride in water. To our chagrin, complete deacylation occurred within a few seconds, as was evidenced in the NMR spectra of the solutions by the appearance of the characteristic C-2 proton of the unsubstituted 1,3-dimethylbenzimidazolium ion at δ 9.1 and the shift of the acetyl singlet from δ 2.9 to 2.0. Removal of water and pyridine under reduced pressure, followed by solvent extraction, left a residue which was quickly identified with an authentic sample of 1,3-dimethylbenzimidazolium chloride, but no trace of acetanilide or of *N*-benzylacetamide was to be found anywhere. In fact, the acetyl group seemed to have disappeared almost entirely. It was located in due course in the trapped volatiles, was rendered nonvolatile with sodium hydroxide, and was authenticated as acetic acid by NMR comparisons and by conversion into crystalline *p*-bromophenacyl acetate,[2] identical with authentic material.

Aqueous solutions of glycine and phenylalanine, as well as of aniline and benzylamine, also brought about rapid deacylation, and in all cases acetic acid and the deacylated benzimidazolium ion were the products. Only when reaction was carried out with benzylamine in water-free dimethyl sulfoxide was *N*-benzylacetamide obtained.

Further experimentation revealed that the quaternary 2-acetylbenzimidazolium ion is quite stable in weakly acidic aqueous solution. Less than 5% deacylation occurs during 3 weeks at pH 2. If the pH is raised to neutrality, however, deacylation is rapid, the half-life at pH 7.7 (HEPES) being no more than 20–30 s. The deacylation rate constant, k_2^{OH}, is about 3×10^6 M^{-1} min^{-1}. At pH 5.2 and 4.5, half-lives were 2.5 and 12 h, respectively, confirming that deacylation is brought about by hydroxide ion, even at concentrations of 10^{-9}–10^{-6} M, and hardly, if at all, by water.

Aniline (0.3 M) and pyridine (0.1 M) produced no detectable increase in the deacylation rate, which was indistinguishable (<5%) over four half-lives from that in buffer (HEPES, pH 7.7; MES, pH 5–6) alone. Rate constants for reaction of these nucleophiles thus cannot be determined in the usual way, but it is easily calculated that they cannot at the outside be greater than 5×10^{-4} (aniline) and 1×10^{-3} (pyridine) M^{-1} min^{-1}. These values contrast sharply with published rate constants[9] for *p*-nitrophenyl acetate, a typical active ester acylating agent. The hydroxide constant is 3000 times greater (pNPA, 1×10^3 M^{-1} min^{-1}), while the aniline and pyridine constants are 50–100 times less (pNPA–aniline, 2.3×10^{-2}; pNPA–pyridine, about 10^{-1} M^{-1} min^{-1}).

That the 2-acetyl-1,3-dimethylbenzimidazolium ion is subject to ready deacylation is not particularly surprising. The 1,3-dimethylbenzimidazolium 2-carbanion should be quite a good leaving group.[3] The C-2 proton of 1,3-dimethylbenzimidazolium salts exchanges rapidly in very weakly basic solution.[4] Analogous quaternary 2-acylthiazolium salts examined in the course of the classic work on the mechanism of function of thiamin 25 years ago are deacylated in neutral water just about as readily as the benzimidazolium compound is.[5] And indeed, the deacylation of 2-acetyl-1,3-dimethylbenzimidazolium iodide by water, alcohols, phenols, and amines had been reported previously,[6] although the conditions utilized were so vigorous as to give no hint as to the facility with which reaction would take place.

What is exceptional, however, is the lack of reactivity toward primary aliphatic and aromatic amine nucleophiles in water, and toward water itself for that matter, in contrast to a reactivity toward the hydroxide ion thousands of times greater than that of a typical active ester and not far short of that exhibited by typical acid anhydrides.

Hydroxide ion is a remarkably poor nucleophile toward acylating agents.[7] Even weakly basic amines such as aniline and *p*-anisidine are acylated quite satisfactorily in aqueous sodium carbonate by such reagents as acetic anhydride and benzoyl chloride, yet if nucleophilic competitiveness merely reflected concentration multiplied by basicity, nothing but hydrolysis products should result.[8] Brönsted plots for hydrolysis and aminolysis reactions of esters show hydroxide 2, 3, even 5 log units off the lines (slopes typically about 0.8) for amines and well off the lines for other oxyanion nucleophiles in many cases.[9] Comparable plots of the present data would have hydroxide not more than 1 log unit at the outside below a line of unit slope or on, or even above, a line of slope 0.9. It has been suggested[10] that the anomalous behavior of hydroxide, which is exhibited to some extent by other strongly basic oxyanions also, might be attributed to a requirement for rate-influencing or rate-controlling desolvation of these strongly solvated ions, and further evidence and cogent arguments continue to appear.[11] Most noticeable, however, is the dearth of exceptions to the anomaly. The low reactivity of hydroxide ion is so commonplace, so ubiquitous, as to seem the norm. As best we can ascertain, the 2-acetyl-1,3-dimethybenzimidazolium ion is the first acylating agent to exhibit the reactivity it properly should toward the hydroxide ion as opposed to other nucleophiles.

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(3) For discussion see: Bruice, T. C.; Benkovic, S. *Bioorganic Mechanisms*; Benjamin: New York, 1966; Vol. 2, pp 214–220.

(4) The C-2 proton cannot be seen in NMR spectra at pH 8 or above.

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(7) See, for example: Jencks, W. P. *Catalysis in Chemistry and Enzymology*; McGraw-Hill: New York, 1969; pp 78–98.

(8) Aniline, K_b (4.6×10^{-10}) × concentration (0.3 M) = 1.4×10^{-10}; OH$^-$ at pH 10, K_b (55.5) × concentration (10^{-4} M) = 55.5×10^{-4}; relative nucleophilic competitiveness should be 4×10^7 in favor of hydrolysis over aminolysis. At higher pH, should be even more so.

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Rapid, Low Activation Energy, Selective, Direct Reactions of Cation Radicals with Nucleophiles. An Experimental Test of Theory

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A number of reactions of cation radicals with nucleophiles are second order in cation radical and first order in nucleophile.[1a,b] When these reactions are studied by homogeneous kinetic techniques the stoichiometry which must be considered is the half-regeneration scheme (1).[2a–e,3ab] The apparent low reactivity of

$$2\mathrm{A}^{\cdot+} + \mathrm{Nu} \rightarrow \mathrm{A}^{+}\text{–}\mathrm{Nu}^{+} + \mathrm{A} \qquad (1)$$

some cation radicals as compared to the corresponding carbocations was noted by Eberson.[4]

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