Inorg. Chem. **1989**, *28*, 4323–4326

Contribution from the Rudjer Boskovič Institute, 41000 Zagreb, Croatia, Yugoslavia,
and Ames Laboratory and the Department of Chemistry, Iowa State University, Ames, Iowa 50011

Kinetics of Reduction of a Series of Imidazolium Ions and Cobalt(III)–Imidazole Complexes by 1-Hydroxy-1-methylethyl Radicals

Andreja Bakac,*,[1a] Vjera Butkovič,[1b] James H. Espenson,*,[1a] Jasna Lovrič,[1b] and Matko Orhanovič*,[1b]

Received April 28, 1989

The rates of electron transfer from $^{\bullet}C(CH_3)_2OH$ to a series of imidazolium ions and to a series of $(NH_3)_5Co(X\text{-}Im)^{3+}$ complexes have been measured. A kinetic competition method based on the homolytic scission of the chromium–carbon bond in $(H_2O)_5CrC(CH_3)_2OH^{2+}$ was used to evaluate rate constants for the reducing agent $^{\bullet}C(CH_3)_2OH$. In both series the rate constants show sensitivity to substituents on the imidazole ring. The rate constants for the free imidazolium ions are correlated by an LFER to the relative electron affinity of the imidazolium ion. The rate constants for the cobalt(III)–imidazole complexes are correlated by the lowest energy d–d absorption band of the complexes.

Introduction

Relatively little information is available concerning the rates and mechanism of electron transfer to N-heterocycles. Our major interest has been centered on the use of the 1-hydroxy-1-methylethyl radical, $^{\bullet}C(CH_3)_2OH$, as a reducing agent. In these cases the rates of reaction were evaluated by the method of "stored free radicals".[2] As far as we are aware, there have been no previous investigations of the reactions in which imidazolium ion and its derivatives are reduced by $^{\bullet}C(CH_3)_2OH$.

In this work we have set out to determine the kinetics of reduction of imidazolium ions and their ring-substituted derivatives ($X\text{-}ImH^+$) by $^{\bullet}C(CH_3)_2OH$. Our goal was to determine (and, if possible, quantify) the structural and electronic factors that influence the kinetic parameters. In that sense this work is an extension of our earlier efforts to study reactions of pyridinium ion derivatives[2b] and their complexes with metal ions (Co, Cr, Ru).[3-5]

Imidazoles are of interest in the context of biological electron transfer. They are also of interest to us because they provide an extensive series of compounds in which the effects of ring substituents can be examined. This is largely an unknown area, since the use of Hammett parameters to effect a correlation is not available.[6] Only in the case of e^-_{aq} has the rate of one-electron reduction of an imidazole been determined, and in that case only for the parent compound itself.[7]

In this work we have measured the kinetics of the reactions between $^{\bullet}C(CH_3)_2OH$ and a series of eight imidazolium ions ($X\text{-}ImH^+$) and a series of five cobalt complexes ($(NH_3)_5Co(X\text{-}Im)^{3+}$). The parameter against which these rates correlated is a measure of the electron affinity of the imidazolium ion, as calculated from the ionization potential and spectroscopic data.

Experimental Section

Materials. Imidazole and its 1-CH_3, 2-CH_3, 4(5)-CH_3 and 4,5-Cl_2 derivatives were purchased from Aldrich. The 1-CH_2CO_2H, 4(5)-CH_3-5(4)-$CONH_2$, and 4(5)-CH_3-5(4)-CN derivatives were used from a previously available stock.[8] The imidazoles from both sources had to be carefully purified in order to obtain reproducible kinetic results. They were purified by sublimation (imidazole and 2-CH_3 and 4(5)-CH_3 derivatives), by distillation (1-CH_3), and by recrystallization from a 50% water–ethanol mixture.

Table I. Characterization of the $[(NH_3)_5Co(N_2C_3H_2XY)](ClO_4)_3$ Complexes

X	Y	λ_1/nm (ϵ/M^{-1} cm^{-1})[a]	λ_2/nm (ϵ/M^{-1} cm^{-1})[a]	% Co found (% calc)
H	H	473 (61.6)[b]	334 (72.6)[b]	11.1 (11.5)
4(5)-CH_3	H	475 (57.2)	330 (92.8)	
1-CH_3	H	475 (63.4)	336 (96.0)[sh]	10.2 (11.2)
2-CH_3	H	478 (63.8)	335 (85.6)[sh]	11.6 (11.2)
4-Cl	5-Cl	480 (58.7)	335 (95.7)	10.0 (10.3)

[a] In water solution. [b] In good agreement with literature data: Harrowfield, J. MacB.; Norris, V.; Sargeson, A. M. *J. Am. Chem. Soc.* **1976**, *98*, 7282.

Cobalt(III) imidazole complexes $[(NH_3)_5Co(N_2C_3H_3X)](ClO_4)_3$ and $[(NH_3)_5Co(N_2C_3H_2XY)](ClO_4)_3$ were prepared[9] by heating the pentaamminea aqua complex with the corresponding imidazole in *N,N'*-dimethylformamide (X = 2-CH_3, Y = X = Cl) or in dmso (all others) and then precipitating the product with sodium perchlorate. The product was recrystallized three to five times from 0.1 M $HClO_4$. Its identity was ascertained by cobalt analysis[10] and by the position and molar absorptivities of the UV–visible absorption maxima, as given in Table I. Note that the ligand-field bands for all of the complexes are quite close to one another.

Triply distilled water was used throughout. Lithium perchlorate (Merck analytical grade) was recrystallized four times from water. Distilled 2-propanol was kept in a dark bottle and redistilled at least weekly. Solutions of $Cr(H_2O)_6^{2+}$ were prepared by zinc amalgam reduction of stock $Cr(H_2O)_6^{3+}$ solutions, which were made from triply recrystallized $[Cr(H_2O)_6](ClO_4)_3$. Air-free conditions were maintained in all the experiments by use of purified nitrogen, which was first passed over a heated copper catalyst and then through a Cr^{2+} scrubbing tower. The source of the aliphatic radical was the organochromium complex $(H_2O)_5CrC(CH_3)_2OH^{2+}$.

Techniques. Kinetic investigations of the reactions of both cobalt(III)-bound imidazoles and free imidazolium ions with 1-hydroxy-1-methylethyl radicals were done spectrophotometrically by use of a Cary 219 instrument. The decrease of absorbance was monitored at 311 nm, the wavelength of maximum absorption of $(H_2O)_5CrC(CH_3)_2OH^{2+}$ (ϵ 2500 M^{-1} cm^{-1}). The reagents competing for the $^{\bullet}C(CH_3)_2OH$ radical (formed by homolysis of the organochromium cation), $Cr(H_2O)_6^{2+}$ and imidazolium ions or Co(III)–imidazole complexes, were used in much higher concentrations than those of the organochromium ions to ensure pseudo-first-order conditions. Rate constants were evaluated from the kinetic data by plots of ln $(D_t - D_\infty)$ versus time.

The stoichiometry of the reaction between the radicals and the cobalt(III) complexes was checked by determination of the cobalt(II) produced.[10]

---

[1] (a) Iowa State University. (b) Rudjer Boskovič Institute.

[2] (a) Espenson, J. H.; Shimura, M.; Bakac, A. *Inorg. Chem.* **1982**, *21*, 2537. (b) Shimura, M.; Espenson, J. H. *Inorg. Chem.* **1983**, *22*, 334.

[3] Bakac, A.; Butkovič, V.; Espenson, J. H.; Marcec, R.; Orhanovič, M. *Inorg. Chem.* **1986**, *25*, 341.

[4] Bakac, A.; Butkovič, V.; Espenson, J. H.; Marcec, R.; Orhanovič, M. *Inorg. Chem.* **1986**, *25*, 2562.

[5] Bakac, A.; Butkovič, V.; Espenson, J. H.; Marcec, R.; Orhanovič, M. *Inorg. Chem.* **1987**, *26*, 3249.

[6] Several successful applications of the Hammett-type relationship to the reactions of imidazoles have been described: (a) Takeuchi, Y.; Kirk, K. L.; Cohen, L. A. *J. Org. Chem.* **1978**, *43*, 3570. (b) Charton, M. *J. Org. Chem.* **1979**, *44*, 903. (c) Charton, M. *J. Org. Chem.* **1965**, *30*, 3346. (d) Grimmett, M. R. *Adv. Heterocycl. Chem.* **1980**, *27*, 241; **1970**, *12*, 103. (e) Grimmett, M. R. In *Comprehensive Heterocyclic Chemistry*; Katritzky, A. R., Rees, C. W., Eds.; Pergamon: Oxford, England, 1984; Vol 5. (f) Lopyrev, V. A.; Larina, L. I.; Vakul'skaya, T. I. *Russ. Chem. Rev.* (*Engl. Transl.*) **1986**, *55*, 411. In the present work, however, the substituents were varied in several positions in the ring, which made it impossible to use any single substituent constant in the analysis.

[7] (a) Braams, R. *Radiat. Biol.* **1966**, *27*, 319. (b) Greenstock, C. L.; Ng, M.; Hunt, J. W. *Adv. Chem. Ser.* **1968**, *No. 81*, 321.

[8] Blazevic, K.; Kajfez, F.; Sunjic, V. *J. Heterocycl. Chem.* **1970**, *7*, 227.

[9] Gould, E. S. *J. Am. Chem. Soc.* **1965**, *87*, 4730.

[10] Kitson, R. F. *Anal. Chem.* **1950**, *22*, 664.

0020-1669/89/1328-4323$01.50/0

Table II. Ranges of the Concentrations Used and the Slopes of the Plots of $(k_{obsd} - k_A)^{-1}$ vs $[Cr^{2+}]/[ImH^+]$ for the Reduction of Imidazolium Ions ($N_2C_3H_3XY^+$) by $^{\bullet}C(CH_3)_2OH$[a]

X	Y	$10^4[Cr^{2+}]$/M	$10^4[ImH^+]$/M	$10^2[Cr^{2+}]/[ImH^+]$	10^{-2} × slope/s[b]
4(5)-CH_3	5(4)-CN	2.6–6.6	2.1–13.6	19–190	0.83
4-Cl	5-Cl	1.9–8.1	16–65	4.4–49	1.21
4(5)-CH_3	5(4)-$CONH_2$	2.0–4.6	10–60	5.0–22	1.96
1-CH_3	H	1.7–8.0	20–79	6.5–12	3.87[c]
4(5)-CH_3	5(4)-H	2.0–10.0	42–116	7.7–17	9.0
H	H	2.1–9.1	8.9–150	2.5–6.0	23.9[c]
1-CH_2COOH	H	1.7–2.5	42–200	1.0–5.3	53.2
2-CH_3	H	2.0–2.4	195–400	0.5–1.6	305[c]

[a] 25.0 °C, $[H^+] = 0.1$ M, and $\mu = 1.0$ M ($HClO_4 + LiClO_4$) in aqueous 1 M 2-propanol. [b] Standard deviation is 3–5%. [c] $[H^+] = 0.01$–1.0 M.

Table III. Ranges of the Concentrations Used and the Slopes of the Plots of $(k_{obsd} - k_A)^{-1}$ vs $[Cr^{2+}]/[Co(III)]$ Obtained for the Reduction of $(NH_3)_5Co(N_2C_3H_2XY)^{3+}$ Complexes by $^{\bullet}C(CH_3)_2OH$[a,b]

X	Y	$10^4[Cr^{2+}]$/M	$10^4[Co(III)]$/M	$[Cr^{2+}]/[Co(III)]$	slope/s[c]
4-Cl	5-Cl	2.7–6.7	2.4–4.7	0.58–1.8	21.7 ± 0.7
2-CH_3	H	2.0–4.8	2.4–6.1	0.34–1.1	135 ± 3
1-CH_3	H	1.7–3.7	3.4–6.1	0.27–0.9	183 ± 5
4(5)-CH_3	H	1.7–3.3	3.6–6.6	0.26–0.9	220 ± 8
H	H	7.9–3.8	3.3–6.3	0.32–1.0	284 ± 6

[a] $N_2C_3H_2XY$ = substituted imidazole. [b] 25.0 °C, $[H^+] = 0.1$ M, and $\mu = 1.0$ M ($HClO_4 + LiClO_4$) in aqueous 1 M 2-propanol. [c] Uncertainties quoted are standard deviations.

Results

Reaction Scheme and Kinetic Equations. There are several reactions involved in the overall reduction scheme. The acidolysis of the organochromium ion (eq 1) has been previously investigated[11,12] and proceeds with a rate constant expressed as $k_A = 3.31 \times 10^{-3} + 4.91 \times 10^{-3}\,[H^+]$ s^{-1} at 25.0 °C and ionic strength 1.0 M.

$$(H_2O)_5CrC(CH_3)_2OH^{2+} \xrightarrow{H_2O,\ H^+} Cr(H_2O)_6^{3+} + HC(CH_3)_2OH \quad (1)$$

This is a background reaction and a limit below which the overall first-order rate constant cannot fall. It is a nonproductive pathway for the reduction reaction, and as such it is a "waste" of the radical.

The second reaction (eq 2) consists of the reversible homolytic dissociation of the chromium–carbon bond. Both rate constants are known from earlier work.[11,13]

$$(H_2O)_5CrC(CH_3)_2OH^{2+} \underset{k_{Cr}}{\overset{k_H,\ H_2O}{\rightleftharpoons}} Cr(H_2O)_6^{2+} + {}^{\bullet}C(CH_3)_2OH \quad (2)$$

The values are $k_H = 0.127$ s^{-1} at 25.0 °C[11] and $k_{Cr} = 5.1 \times 10^7$ M^{-1} s^{-1} at 22 ± 3 °C.[13]

Self-reactions between two free radicals are not important under any of the conditions employed, since added quantities of the reactive Cr^{2+} and X-ImH^+ or $(NH_3)_5Co(X\text{-}Im)^{3+}$ ions serve to keep the radical concentrations very low. The reactions of interest are shown in eq 3a and 3b.

$$^{\bullet}C(CH_3)_2OH + X\text{-}ImH^+ \rightarrow (CH_3)_2CO + X\text{-}ImH^{\bullet} + H^+ \quad (3a)$$

$$^{\bullet}C(CH_3)_2OH + (NH_3)_5Co(X\text{-}Im)^{3+} \xrightarrow{H^+} (CH_3)_2CO + Co^{2+} + 5NH_4^+ + X\text{-}ImH^+ \quad (3b)$$

In view of the very low concentration of free radicals, the steady-state approximation is applicable. The rate of disappearance of the organochromium complex is thus given by

$$\frac{-d[(H_2O)_5CrC(CH_3)_2OH^{2+}]}{dt} = \left(k_A + \frac{k_H k_3[X\text{-}ImH^+]}{k_3[X\text{-}ImH^+] + k_{Cr}[Cr^{2+}]}\right)[(H_2O)_5CrC(CH_3)_2OH^{2+}] \quad (4)$$

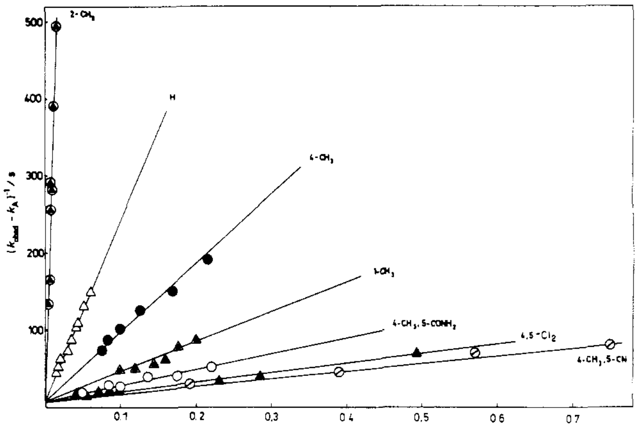

Figure 1. Plots according to eq 5 for the reactions of imidazolium ions with $^{\bullet}C(CH_3)_2OH$.

Table IV. Rate Constants for the Reduction of the Imidazolium Ions ($N_2C_3H_3XY^+$) and $(NH_3)_5Co(N_2C_3H_2XY)^{3+}$ Complexes by $^{\bullet}C(CH_3)_2OH$[a]

X	Y	$N_2C_3H_3XY^+$ $10^{-6}k_{3a}$/M^{-1} s^{-1}	$(NH_3)_5Co(N_2C_3H_2XY)^{3+}$ $10^{-6}k_{3b}$/M^{-1} s^{-1}
4(5)-CH_3	5(4)-CN	4.8	
4-Cl	5-Cl	3.3	18.5
4(5)-CH_3	5(4)-$CONH_2$	2.05	
1-CH_3	H	1.05	2.2
4(5)-CH_3	5(4)-H	0.45	1.8
H	H	0.17	1.4
1-CH_2COOH	H	0.075	
2-CH_3	H	0.013	3.0

[a] 25.0 °C, $[H^+] = 0.1$ M, and $\mu = 1.0$ M ($HClO_4 + LiClO_4$) in aqueous 1 M 2-propanol.

Provided experiments are done with initial concentrations of chromium(II) and imidazole species much higher than that of the organochromium complex, the reaction will follow pseudo-first-order kinetics with the quantity in parentheses in eq 4 being k_{obsd}.

Imidazolium Ions. These reactions were studied over the concentration ranges listed in Table II. In every case the data fit the pseudo-first-order kinetics well. The values of k_{obsd} were correlated by a rearranged form of eq 4 in which the inverse of the difference of the rate constants is a linear function of the concentration ratio $[Cr^{2+}]/[X\text{-}ImH^+]$, as shown in eq 5. The value of k_3 is the only unknown in this equation, and its value can

---

(11) Kirker, G. W.; Bakac, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1982**, *104*, 1249.

(12) Schmidt, W. A.; Swinehart, J. H.; Taube, H. *J. Am. Chem. Soc.* **1971**, *93*, 1116.

(13) Cohen, H.; Meyerstein, D. *Inorg. Chem.* **1974**, *13*, 2434.

$$\frac{1}{k_{\text{obsd}}-k_{\text{A}}} = \frac{1}{k_{\text{H}}} + \frac{k_{\text{Cr}}}{k_3 k_{\text{H}}}\frac{[\text{Cr}(\text{H}_2\text{O})_6^{2+}]}{[\text{X-ImH}^+]} \qquad (5)$$

be calculated from the slope of the line. Such plots are shown for the imidazolium ions in Figure 1. The slopes are given in Table II.

Cobalt(III)-Imidazole Complexes. The conditions under which the kinetic measurements were made are given in Table III. The plots according to eq 5 are shown in Figure 2. The rate constants for the cobalt-imidazole complexes and for the imidazolium ions are summarized in Table IV.

The stoichiometry of the reaction between cobalt imidazole complexes and $^•C(CH_3)_2OH$ was checked by determination of $[Co^{2+}]$ in kinetic experiments using high concentrations of $(H_2O)_5CrC(CH_3)_2OH^{2+}$. In a typical experiment with $(NH_3)_5Co(Im)^{3+}$ or $(NH_3)_5Co(2\text{-}CH_3Im)^{3+}$ the initial concentration of $CrC(CH_3)_2OH^{2+}$ was 5.3 ± 0.4 mM. Depending on the $[Cr^{2+}]/[Co(III)]$ ratio, 20–27% of the organochromium ion underwent acidolysis and the rest, via $^•C(CH_3)_2OH$, reacted with the Co(III) producing Co^{2+}.

Discussion

The reaction of imidazolium ions with the reducing $^•C(CH_3)_2OH$ radical is somewhat slower than the reduction of the pyridinium ions with the same radical.[2b] The lower reducibility of the imidazolium series was to be expected on the basis of the kinetic data for the reduction of pyridine and imidazole with hydrated electrons.[7] The protonated forms of both species are reduced by e^-_{aq} at close to diffusion-controlled rate, which masks any possible difference in reducibility, but the rate constants for the less reactive unprotonated species differ by more than a factor of 100, imidazole being the less reactive.

In view of the inapplicability of the Hammett relationship[6] to imidazoles, and the lack of the available one-electron reduction potentials, we sought parameters that would allow meaningful correlation with the kinetic data in order to (a) ascertain that the reaction with $^•C(CH_3)_2OH$ is indeed reduction and (b) establish the mechanism(s) of reduction of metal-imidazole complexes (attack at imidazole or at the metal), as was done earlier for the pyridine analogues.[3-5] The parameter we use in this work is defined in eq 6, where E_i stands for the ionization potential of

$$\Delta E = E_i - E_{\pi-\pi^*} \qquad (6)$$

the imidazole and $E_{\pi-\pi^*}$ the spectroscopic energy of the π–π^* transition of the imidazolium ion in aqueous solution. The difference ΔE is thus a relative measure of the electron affinity of the imidazolium ions under the (reasonable) assumption that the π–π^* transition and the one-electron reduction populate the same π^* molecular orbital. The use of the gas-phase ionization potentials of the unprotonated species, in place of the oxidation potentials of the protonated species, limits the correlations with the derived parameter ΔE to a series of closely related compounds, such as imidazolium ions, for which the contribution of protonation and solvation effects to electron affinity is expected to be approximately constant. The pertinent data are listed in Table V.

Figure 3 shows a plot of log k against ΔE for all the imidazolium ions studied. Qualitatively the data follow the expected trend and the rate constants increase approximately linearly with ΔE. Also shown in Figure 3 are the data for a series of pyridinium ions. The correlation is again approximately linear and parallels that obtained for the imidazolium ions.

In our previous work[2] we have established that $^•C(CH_3)_2OH$ reduces the pyridinium ions and that the kinetic data correlate well with the Hammett substituent constant σ, such that the electron-withdrawing substituents accelerate the reaction. The successful correlation with ΔE in Figure 3 for the pyridinium ions for which the data were available indicates that the parameter ΔE correctly predicts the reducibility (electron affinity) within the series. The similarity of the correlations obtained for the imidazolium and the pyridinium ions thus strongly supports our original assertion that the reaction of the former with $^•C(CH_3)_2OH$ is also reduction.

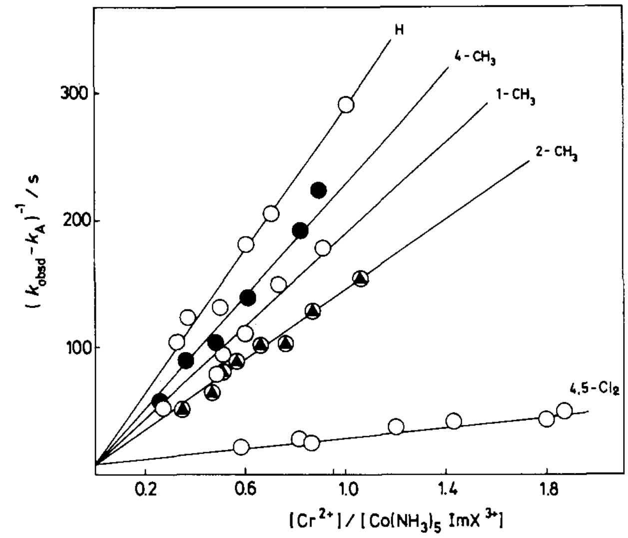

Figure 2. Plots according to eq 5 for the reactions of $(NH_3)_5Co(X\text{-}Im)^{3+}$ with $^•C(CH_3)_2OH$.

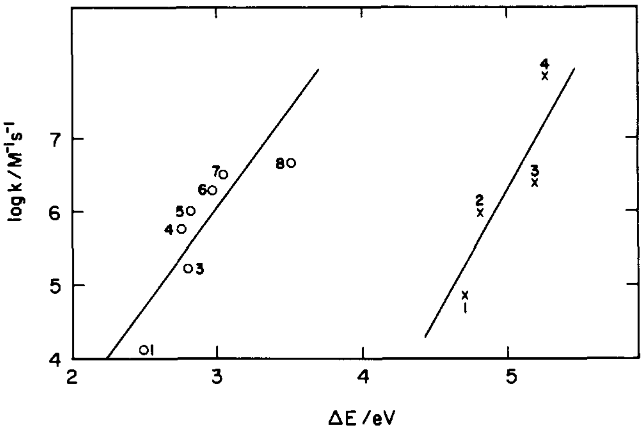

Figure 3. Plots of the logarithms of the rate constants for the reaction of $^•C(CH_3)_2OH$ with imidazolium (O) and pyridinium (X) ions against ΔE of eq 6. The points are labeled as in Table V.

From the two correlations in Figure 3 it follows that for a given value of ΔE the imidazolium ions would be reduced more easily than the pyridiniums. This (hypothetical) situation is contrary to the expectations on the basis of the results of the reduction of the two parent species by e^-_{aq}. We believe that the displacement of the two lines in Figure 3 does not represent the difference in intrinsic reactivities. Indeed, the experimental rate constants for the unsubstituted pyridinium ion is *higher* than that for the imidazolium, as expected. Rather, the upward shift of the imidazolium series probably only illustrates that the *absolute* values of ΔE have little significance, owing to the approximations used, and that the contribution of the solvation and protonation to the true oxidation potential differs significantly for the two series.

The available data are insufficient to distinguish between outer-sphere electron transfer and initial addition of $^•C(CH_3)_2OH$ to the imidazolium ring. Very few reactions of imidazoles with C-centered radicals have been studied, but from the limited data available it appears that the nucleophilic radicals attack preferentially or exclusively at the C2 carbon, the most electron-deficient site in the molecule.[6d,14] This also seems to be the most obvious site for attack by the strongly reducing $^•C(CH_3)_2OH$. Additional support for this proposition comes from the analysis of the kinetic data in Table IV. The rate constants for the unsubstituted and the 1-, 4-, and 5-substituted imidazolium ions all fall in the range $(1.7\text{–}48) \times 10^5$ M^{-1} s^{-1}, whereas the 2-CH_3 derivative has $k = 1.3 \times 10^4$ M^{-1} s^{-1}. The blocking of the C2 thus severely inhibits

---

(14) Begg, C. G.; Grimmett, M. R.; Lee, Y. M. *Aust. J. Chem.* **1973**, *26*, 415.

Table V. Ionization Potentials, Spectroscopic Data, and Logarithms of the Rate Constants for the Reactions of $^{\bullet}C(CH_3)_2OH$ with Imidazolium Ions ($N_2C_3H_3XY^+$) and Pyridinium Ions ($NC_5H_5X^+$)

reacn no.	X	Y	log (k/M^{-1} s^{-1})	λ_{max}/nm[a]	E_i/eV[b]	$E_{\pi-\pi^*}$/eV	ΔE/eV[c]
			$N_2C_3H_3XY^+$				
1	2-CH_3	H	4.12	205	8.54[d]	6.05	2.49
2	1-CH_2COOH	H	4.88	209		5.93	
3	H	H	5.23	206	8.81[d]	6.02	2.79
4	4-CH_3	H	5.65	212	8.57[d]	5.82	2.75
5	1-CH_3	H	6.03	211	8.69[d]	5.88	2.81
6	4(5)-CH_3	5(4)-$CONH_2$	6.31	225	8.47[e]	5.51	2.96
7	4-Cl	5-Cl	6.52	220	8.67[e]	5.64	3.04
8	4(5)-CH_3	5(4)-CN	6.68	223	9.07[e]	5.56	3.51
			$NC_5H_5X^+$				
1	4-CH_3		4.86[f]	263	9.41[h]	4.71	4.70
2	H		5.98[f]	255	9.66[h]	4.85	4.81
3	4-Cl		6.41[g]	257	10.01[h]	4.81	5.19
4	3-Cl		7.87[g]	271	9.83[h]	4.57	5.25

[a] In 0.1 M H^+ aqueous solutions. [b] First ionization potential in gas phase. [c] $\Delta E = E_i - E_{\pi-\pi^*}$. [d] Klasinc, L.; Ruscic, B.; Kajfez, F.; Šunjić, V. *Int. J. Quantum Chem.* **1978**, *5*, 367. [e] Kovac, B. Personal communication. [f] Reference 2b. [g] Reference 3. [h] Klasinc, L.; Novak, I.; Scholz, M.; Kluge, G. *Croat. Chem. Acta* **1978**, *51*, 43.

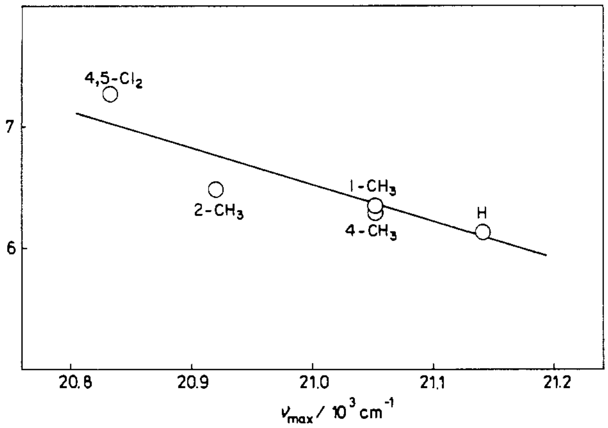

Figure 4. Plot of the logarithms of the rate constants for the reduction of the $(NH_3)_5Co(X\text{-}Im)^{3+}$ complexes by $^{\bullet}C(CH_3)_2OH$ against the position of the lowest energy d–d band.

the reaction, as expected if this is the most reactive site in the molecule. However, 2-methylimidazolium ion is also the least reducible thermodynamically, as shown by its low ΔE value. The data thus do not allow a clear distinction between electron transfer and attack at C2.

The initial products of the reactions of $^{\bullet}C(CH_3)_2OH$ with the imidazolium ions can disappear either in radical self-reactions or in subsequent reactions with Cr^{2+}. This point has not been checked experimentally.

The reaction of $^{\bullet}C(CH_3)_2OH$ with the cobalt complexes $(NH_3)_5Co(X\text{-}Im)^{3+}$ takes place according to eq 3b. The 1:1 stoichiometry and the products are analogous to those obtained in the corresponding reactions with the cobalt-pyridine complexes.[3] In the latter case we argued that the reduction takes place at the cobalt rather than pyridine on the basis of the small Hammett ρ value. In view of the lack of suitable parameters needed for such a correlation in the case of the cobalt–imidazole complexes, we looked for other clues to help us identify the reactive site.

The rate constants for the five cobalt complexes cover a narrow range, (3–18) × 10^6 M^{-1} s^{-1}. The reactivity of the same five imidazolium ions varies by a factor of 250, k = (1.3–330) × 10^4 M^{-1} s^{-1}. This difference in sensitivity toward substituents on the imidazole ring strongly suggests that the reduction of $(NH_3)_5Co(X\text{-}Im)^{3+}$ takes place by direct electron transfer to cobalt. The most dramatic case, and one that argues most strongly in favor of direct electron transfer, is again that of 2-methylimidazole. Despite the extremely low reactivity of the free ion, the cobalt complex has a rate constant comparable to those for all the other complexes.

If the reduction of the $(NH_3)_5Co(X\text{-}Im)^{3+}$ complexes is indeed an electron transfer to cobalt, one might expect a correlation with the position of the lowest energy d–d band,[15] which is taken as a qualitative indicator of the ease with which an electron is placed in the antibonding d orbital. Such a plot, shown in Figure 4, shows that there is indeed a correlation between the kinetic and spectroscopic data.

All the indicators thus point to direct reduction of the cobalt–imidazole complexes, as was observed earlier in the pyridine series.[3] This can be easily rationalized by the fact that the cobalt(III) center is more reducible than the heterocyclic ligands of either series. It would be interesting to see whether the chromium(III)–imidazole complexes parallel the chromium(III)–pyridine series, where the initial attack by the radical takes place at the pyridine ring.[4] Since the free imidazolium ions are reduced somewhat more slowly than the free pyridiniums, there is a possibility that even the chromium–imidazole complexes might react by electron transfer to chromium.

Acknowledgment. This work was supported in part by the U.S. Department of Energy through the Joint U.S.-Yugoslav Board for Scientific Cooperation, by the Research Council (SIZZ) of S.R. Croatia, and by the U.S. Department of Energy, Office of Basic Energy Sciences, Chemical Sciences Division, under Cntract W-7405-Eng-82. We are grateful to Dr. Vitomir Šunjić for supplying us with some of the imidazoles, to Dr. Radovan Marcec for preparation of a couple of the cobalt(III)–imidazole complexes, and to Dr. Branka Kovač for making available unpublished data on ionization potentials for some of the imidazoles.

---

(15) Kusaba, K.; Ogino, H.; Bakac, A.; Espenson, J. H. *Inorg. Chem.* **1989**, *28*, 970.