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Photochemical Generation of Alkyl Radicals and Their Reactions with Methyl Viologen Radical Cation and with Transition-Metal Complexes in Aqueous Solution

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The irradiation of aqueous solutions of $RCo([14]aneN_4)(H_2O)^{2+}$ (R = CH_3, C_2H_5, 1-C_3H_7, CH_2Cl, CH_2Br, CH_2OCH_3) with visible light, $\lambda \leq 500$ nm, results in the homolysis of the cobalt–carbon bond. These complexes are quite unreactive toward a variety of dealkylating and redox reagents and thus represent a convenient source of small unstabilized carbon-centered radicals in the presence of potential substrates. The radicals react rapidly with the methyl viologen radical cation, $k_{MV} = (1\text{–}2) \times 10^9\ M^{-1}\ s^{-1}$. The kinetics of the formation of RCr^{2+} and $RCo([14]aneN_4)(H_2O)^{2+}$ in the reactions of radicals with Cr^{2+} and $Co([14]aneN_4)(H_2O)_2{}^{2+}$, respectively, were studied by using MV^+ as a probe. The respective rate constants have values $k_{Cr} = (1.9\text{–}2.4) \times 10^8\ M^{-1}\ s^{-1}$ and $k_{Co} = (1\text{–}2) \times 10^7\ M^{-1}\ s^{-1}$ for all the radicals examined.

Introduction

Despite the abundance of methods available to chemists for the generation of free radicals,[1] there is no general method that would produce useful concentrations (10^{-6}–10^{-5} M) of small hydrocarbon radicals in a short time (<1 μs) in the presence of desired solutes for direct kinetic determinations. There are many factors responsible for this situation. The radical precursors and the solutes have to be chemically compatible; the harsh conditions that are sometimes required for the generation of the radicals, especially by thermal methods, severely limit the choice of substrates; UV photochemical methods impose specific requirements on the UV spectra of all the species involved and also require that the substrates and products be photochemically inert.

Pulse radiolysis[2] is certainly the most useful direct method for the kinetic studies of radical reactions, especially in aqueous solutions. The technique is, however, available only in a few laboratories. Even then, it is not free of problems when it comes to the formation of small hydrocarbon radicals with the exception of $CH_3{}^{\bullet}$. The most straightforward precursors, dialkyl sulfoxides (eq 1),[3] are not available commercially, and the preparation involves the handling of the extremely malodorous sulfides.

$$OH^{\bullet} + R_2SO \rightarrow R^{\bullet} + RSO_2H \qquad (1)$$

The reduction of alkyl halides by hydrated electrons produces the alkyl radicals cleanly (eq 2), but the OH radicals and hydrogen atoms, which are also produced in the pulse, have to be scavenged by reagents that yield less reactive radicals. *tert*-Butyl alcohol is often used, but the resulting $HOC(CH_3)_2CH_2{}^{\bullet}$ itself reacts with a number of substrates, especially metal ions, and may interfere with the study of the reactions of interest.

$$e_{aq}{}^- + RX \rightarrow R^{\bullet} + X^- \qquad (2)$$

The hydrogen atom abstraction from hydrocarbons by OH radicals (eq 3) is limited to compounds that have a relatively high solubility in H_2O and preferably only one kind of reactive carbon–hydrogen bonds.

$$RH + OH^{\bullet} \rightarrow R^{\bullet} + H_2O \qquad (3)$$

Photochemical methods for the generation of free radicals are quite widespread. Owing to the limitations mentioned earlier, a large number of radical precursors are needed to cover a wide range of spectral properties and chemical and photochemical reactivity of the potential reagents. The quantum yield of the radicals produced on photolysis of azoalkanes in the 300–400-nm range is dependent on the solvent; in water the yields are, unfortunately, close to zero.[4] Other standard radical precursors not only require the UV irradiation but are often difficult to prepare and handle (peroxides and peresters),[5] or they only work for a limited number of alkyl groups (ketones and aldehydes).[1e,6,7] The photochemistry of aldehydes is also wavelength dependent.[1e] The coordination complexes of cobalt(III), such as $Co(NH_3)_5O_2CR^{2+}$, also yield $R^{\bullet}$ under certain conditions.[8] The redox reactivity of these complexes, however, limits their usefulness in the presence of reducing substrates.

The photolysis of most alkyl–transition-metal complexes yields carbon-centered radicals and metallic fragments.[9] The organocobalt complexes containing macrocyclic ligands seem to be especially useful as radical precursors owing to the existence of moderately strong absorption bands in the visible region of the spectrum. Thus, irradiation into the ~450-nm band of the organocobaloximes yields the radicals and cobalt(II) (eq 4).[9-14] The reverse of reaction 4 can be prevented by working in acidic solutions where $Co(dmgH)_2L$ decomposes rapidly according to eq 5.[15]

$$\begin{gathered} RCo(dmgH)_2L \xrightarrow{h\nu} R^{\bullet} + Co(dmgH)_2L \\ L = H_2O,\ py,\ CH_3OH,\ \text{etc.} \end{gathered} \qquad (4)$$

$$Co(dmgH)_2L + 2H^+ \rightarrow Co^{2+} + 2dmgH_2 + L \qquad (5)$$

This method has been used recently in the preparation of a series of $RCo([14]aneN_4)H_2O^{2+}$ complexes,[16] which turned out to be themselves an excellent source of primary hydrocarbon radicals

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(10) dmgH is the monoanion of dimethylglyoxime (2,3-butanedione dioxime).

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and substituted analogues. These complexes are chemically quite unreactive but homolyze readily upon irradiation with visible light, $\lambda \leq 500$ nm.

In this paper we demonstrate the usefulness of the $RCo([14]aneN_4)H_2O^{2+}$ complexes as photochemical sources of radicals in a direct determination of the kinetics of the reactions of carbon-centered radicals with MV^+, Cr^{2+}, and $Co([14]aneN_4)^{2+}$ in aqueous solutions.

Experimental Section

Materials. Methyl viologen (1,1′-dimethyl-4,4′-bipyridinium ion, abbreviated MV^{2+}) was purchased as the dichloride salt (Aldrich) and recrystallized three times from methanol. Aqueous solutions of MV^{2+} containing 1–5 mM $HClO_4$ were prepared under argon and converted to MV^+ by reduction on Zn/Hg. In several experiments MV^{2+} was reduced photochemically in the presence of 0.2 M 2-propanol and 0.2 M acetone. The two reduction methods yielded solutions that were kinetically indistinguishable. Solutions of MV^+ were used within 20 min of their preparation.

Solutions of $Co([14]aneN_4)(H_2O)_2{}^{2+}$ were prepared by mixing deaerated aqueous solutions of Co^{2+} and $[14]aneN_4$ (Aldrich) in equimolar amounts. After the complex formation was complete (~10 min), the resulting solution was acidified to 0.05 M $HClO_4$. The complex was then transferred anaerobically to a flask containing amalgamated zinc and kept in ice. The UV–visible spectrum of such solutions showed a maximum at 560 nm (ϵ 21.5 M^{-1} cm^{-1}), in good agreement with the literature spectrum.[17]

The organocobalt complexes $RCo([14]aneN_4)(H_2O)^{2+}$ were prepared as the perchlorate, hexafluorophosphate, or trifluoromethanesulfonate salts according to the published procedure.[16] Stock solutions of Cr^{2+} were prepared by the Zn/Hg reduction of 0.02 M Cr^{3+} in 0.02 M $HClO_4$.

Product Analysis. The gaseous products were analyzed by gas chromatography. A Hewlett-Packard 5790 gas chromatograph, equipped with a VZ-10 column (Alltech), was employed in these experiments. The retention times were determined by use of the commercial gases (Matheson).

The photolysis of aqueous solutions of $C_2H_5Co([14]aneN_4(H_2O)^{2+}$ yielded identical proportions of C_2H_4, C_2H_6, and C_4H_{10}, irrespective of whether the gas or the solution was sampled for the analysis. The same reaction in nonaqueous solvents (dmso, CH_3CN, acetone, 2-propanol) yielded higher proportions of butane in the gas than in solution. Also, the actual ratio (ethane + ethylene)/butane changed with time as more gas was liberated from the solution. Only a qualitative statement on the products of this reaction in nonaqueous solvents is thus made under Results.

Kinetic Procedures. All the reactions were studied by use of the previously described[18] laser flash photolysis system. The dye used was LD 490 (Exciton). The kinetics were monitored at 600 nm where $\epsilon_{MV^+} = 1.37 \times 10^4$ M^{-1} cm^{-1}.[19] The concentration of the radicals produced under a given set of conditions was determined from the absorbance change at 600 nm under conditions where >95% of the radicals were scavenged by MV^+. The rate constants for the reactions of the radicals with MV^+ were evaluated directly from the absorbance–time traces at 600 nm. The reactions with the metal complexes, Cr^{2+} and $Co([14]aneN_4)(H_2O)_2{}^{2+}$, are not accompanied with acceptably large absorbance changes in the concentration range suitable for the kinetic determinations. The kinetics were thus studied by use of MV^+ as a probe in analogy to the well-known diphenylmethanol probe.[1f,20] This method allows the spectrophotometric kinetic studies to be conducted on reactions that themselves involve little or no absorbance change at the monitoring wavelength by introducing an additional reagent whose reaction with the desired substrate involves a significant absorbance change. In that case, for the reaction of Cr^{2+} with radicals $R^\bullet$ as an example, the expression for k_{obsd} is given by eq 6. The term k_0 refers to the loss of the radical

$$k_{obsd} = k_0[R^\bullet] + k_{MV}[MV^+] + k_{Cr}[Cr^{2+}] \tag{6}$$

in the self-reactions. The latter is a second-order process, and strictly speaking, its significance changes during the course of the runs. This, however, caused no problems with the kinetic analyses, since the contribution of the first term in eq 6 was kept at the minimum by working at low concentrations of the radicals (2–4 μM).

The values of the term $k_{Cr}[Cr^{2+}]$ were calculated at different concentrations of Cr^{2+} as the difference between the observed pseudo-first-order rate constants obtained in the presence and absence of Cr^{2+}, respectively, at the given concentrations of MV^+ and $[R^\bullet]_0$. In practice, the plot of k_{obsd} vs $[MV^+]$, obtained in the absence of Cr^{2+}, served as a source of the correcting term $\{k_0[R^\bullet] + k_{MV}[MV^+]\}$. The kinetics of the reactions of the radicals with $Co([14]aneN_4)(H_2O)_2{}^{2+}$ were determined by the same method.

All the experiments were conducted under strictly air-free conditions by use of the standard syringe–septa methods and an atmosphere of argon. No attempt was made to keep the ionic strength constant, since all the reactions studied involve neutral carbon-centered radicals.

Results

Photohomolysis of $RCo([14]aneN_4)(H_2O)^{2+}$. The visible spectra of the organocobalt complexes used in this work exhibit maxima at 460–490 nm (ϵ 70–90 M^{-1} cm^{-1}) and 360–380 nm (ϵ = 100–120 M^{-1} cm^{-1}) in neutral and acidic aqueous solutions.[16] Despite the low molar absorptivities, these complexes produce high concentrations of the radicals when irradiated with visible light (eq 7).

$$RCo([14]aneN_4)H_2O^{2+} \xrightarrow[H_2O]{h\nu} R^\bullet + Co([14]aneN_4)(H_2O)_2{}^{2+} \tag{7}$$

Under our experimental conditions a 1×10^{-4} M solution of $RCo([14]aneN_4(H_2O)^{2+}$ would typically yield 3–4 μM $R^\bullet$ when flashed with the 490-nm beam of laser light. This is consistent with the previous observation that the irradiation of $CH_3Co([14]aneN_4)(H_2O)^{2+}$ causes homolysis of the cobalt–carbon bond as the exclusive process irrespective of the excitation wavelength.[21] The quantum yield of 0.3 was reported for this reaction.[21]

The photolysis of aqueous solutions of the methyl complex yields predominantly ethane, as expected from the self-reaction of the methyl radicals. Trace amounts of methane were also found. Under similar conditions $C_2H_5Co([14]aneN_4)(H_2O)^{2+}$ yields ethane, ethylene, and butane in a relative ratio of 1:1:2.25. This is again consistent with the formation and subsequent self-reactions of ethyl radicals in aqueous solution.[22]

The photolysis of $RCo([14]aneN_4)(H_2O)^{2+}$ in oxygenated solutions causes a significant absorbance increase at λ 380 nm owing to the formation of the peroxocobalt products.[21,23] The latter are known to form rapidly from $Co([14]aneN_4)(H_2O)_2{}^{2+}$ and O_2.[23] The only absorbance changes observed upon flashing the air-free solutions correspond to the loss of $RCo([14]aneN_4)(H_2O)^{2+}$.

In the presence of added Cr^{2+} an absorbance increase was noted at ~300 and ~400 nm, consistent with the formation of RCr^{2+} according to eq 8. This reaction was confirmed and quantified

$$R^\bullet + Cr^{2+} \xrightarrow{k_{Cr}} RCr^{2+} \tag{8}$$

by irradiating a solution containing 4.6 mM $ClCH_2Co([14]aneN_4)(H_2O)^{2+}$ and 24 mM Cr^{2+} in 0.03 M $HClO_4$ with use of a sun lamp. The irradiation was interrupted several times to record the UV–visible spectrum of the solution. The reaction proceeded cleanly and showed isobestic points at 512 and 440 nm. The final spectrum, obtained after about 30 min of irradiation, matched exactly that of 4.7 mM $ClCH_2Cr^{2+}$.[24] Thus, the photolysis of $ClCH_2Co([14]aneN_4)(H_2O)^{2+}$ proceeds exclusively by the homolytic path of eq 7. A solution identical with that described above is stable in the dark for at least 0.5 h.

Photolysis in Nonaqueous Solvents. The complexes $[RCo([14]aneN_4)(H_2O)](PF_6)_2$ are readily soluble in solvents other than water. (The same is expected to be true for the trifluoromethanesulfonate salts.) The 490-nm laser photolysis of 10^{-3}–10^{-2} M solutions of the ethyl complex in acetone, acetonitrile, dimethyl sulfoxide, and 2-propanol yields in each case ethane, ethylene, and butane. The first two are present in approximately equimolar

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Table I. Summary of the Rate Constants (M^{-1} s^{-1}) for the Reactions of Carbon-Centered Radicals with MV^+, Cr^{2+}, and $Co([14]aneN_4)(H_2O)_2^{2+}$ [a]

radical	$10^{-9}k_{MV}$ [b]	$10^{-8}k_{Cr}$ [c]	$10^{-7}k_{Co}$ [d]
CH_3	1.2	2.2	1.6
C_2H_5	1.0	1.9	1.1
C_3H_7	1.2	2.2	
CH_2OCH_3	1.1	2.3	
CH_2Cl	1.4	2.4	
CH_2Br	2.1	2.2	

[a] Conditions: 24 ± 1 °C, $[H^+]$ = 2–20 mM, $[R^\bullet]$ = 2–4 μM, $[MV^+]$ = (0.1–1) × 10^{-4} M. [b] ±10%. [c] ±20%. [d] ±30%.

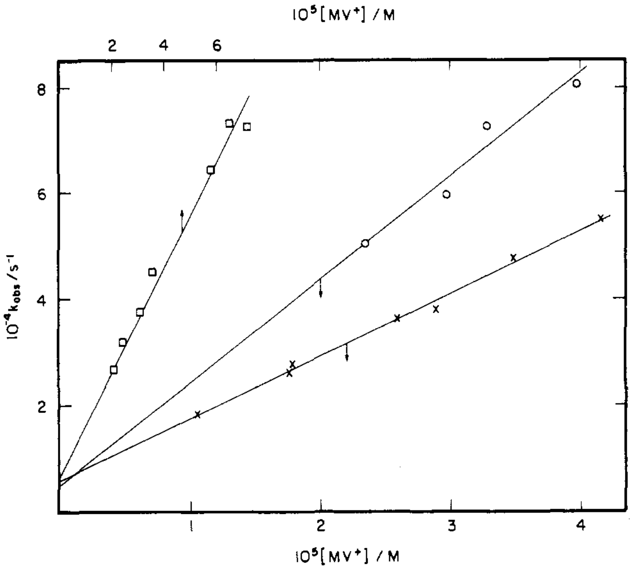

Figure 1. Plot of k_{obsd} against the concentration of MV^+ for the reaction of MV^+ with $^\bullet CH_3$ (crosses), $^\bullet CH_2Br$ (circles), and $^\bullet C_2H_5$ (squares).

amounts, as expected if they are formed by disproportionation of the ethyl radicals. Owing to the high concentrations of the radicals produced in the flash in these reactions, 10^{-5}–10^{-4} M, no hydrogen abstraction from the solvent is observed. The slow photolysis of an acetonitrile solution in the room light yielded predominantly ethane, consistent with the hydrogen abstraction from the solvent by the low steady-state concentrations of the radicals produced under these conditions.

The chemical reactivity of the complexes $RCo([14]aneN_4)(H_2O)^{2+}$ toward dealkylating reagents is quite low. For example, a 1 mM solution of the methyl complex stays unchanged for at least several minutes in the presence of 0.01 M Hg^{2+} or 1 mM Br_2. The transfer of the methyl group to Cr^{2+} takes place with a rate constant of ~0.2 M^{-1} s^{-1}.[25] The ethyl complex reacts even more slowly, $k < 1 \times 10^{-4}$ M^{-1} s^{-1}. There is no reaction between the chloromethyl derivative and 3 mM Br_2 in 6 h.

Reactions of Radicals with MV^+. The stability of the acidic ($[H^+] < 0.01$ M) aqueous solutions of MV^+ (10^{-4}–10^{-5} M) is unaffected by the presence of $\le 2 \times 10^{-4}$ M $RCo([14]aneN_4)(H_2O)^{2+}$ in the dark for any of the R groups listed in Table I. Upon the flashing of such solutions with the 490-nm light, the absorbance at the 600-nm maximum of MV^+ decreases rapidly by an amount that is proportional to the initial concentration of the radical precursor and the energy of the flash. These observations are consistent with the reactions of eq 9. The kinetics of these reactions follow the rate law of eq 10 and 11. The values

$$R^\bullet + MV^+ \xrightarrow{k_{MV}} \text{products} \tag{9}$$

$$-\frac{d[MV^+]}{dt} = -\frac{d[R^\bullet]}{dt} = k_{obs}[R^\bullet] \tag{10}$$

$$k_{obs} = k_{MV}[MV^+] \tag{11}$$

of k_{MV} were obtained as slopes of the plots of k_{obs} vs $[MV^+]$, as illustrated in Figure 1. The small intercepts confirm that only a small fraction of the radicals reacted in self-reactions. The rate constants k_{MV} (Table I) are independent of $[H^+]$ in the pH range 1–7.

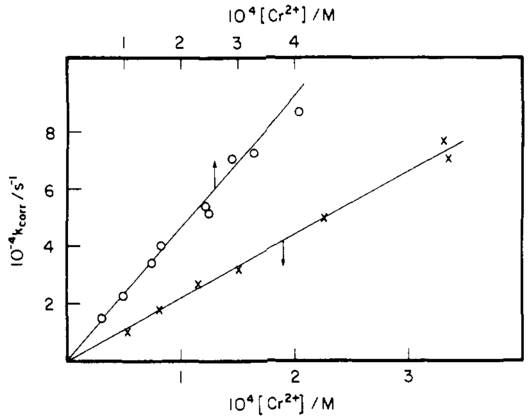

Figure 2. Plot of k_{corr} against the concentration of Cr^{2+} for the reaction of Cr^{2+} with $^\bullet CH_3$ (crosses) and $^\bullet CH_2OCH_3$ (circles).

The GC analysis was performed on the gas above the solutions that were exposed to a number of flashes necessary to cause most, but not all, MV^+ to react with the radicals. For R = CH_3 no gaseous product was observed except for traces of ethane produced in the competing dimerization of the radicals. An identical observation was made earlier in the reaction of MV^+ with thermally generated methyl radicals.[26]

Most of the gaseous products (ethane, ethylene, and butane) found in the reaction of MV^+ with $C_2H_5^\bullet$ are also derived from the radical self-reactions. However, the yields of ethylene were persistently higher (by a factor of 2–3) than those of ethane. A comparison of the GC peak areas obtained for solutions containing (0.5–1) × 10^{-4} M MV^+ with that of a blank containing no MV^+ showed that under our experimental conditions ~25% of the ethyl radicals underwent dimerization and disproportionation, ~70% yielded no gaseous products, and ~5% produced ethylene. A detailed analysis of the nongaseous products is unfortunately not feasible at the low concentration levels needed to prevent significant dimerization[27] and light absorption by MV^+ ($\epsilon_{490} = 2.4 \times 10^3$ M^{-1} cm^{-1}).

Reactions of Radicals with Cr^{2+}. The disappearance of the radicals, monitored as the loss of absorbance at 600 nm, is accelerated in the presence of Cr^{2+} owing to reaction 8, which yields the organochromium complexes CrR^{2+}. All the experiments were conducted in the presence of a pseudo-first-order excess of both MV^+ and Cr^{2+}. Under these conditions the rate law of eq 6 is applicable. The observed rate constants were corrected for the contribution of the first two terms as described in the Experimental Section. The values thus obtained, k_{corr}, are plotted against the concentration of Cr^{2+} in Figure 2. The plots are linear with intercepts close to zero in all the cases. The slopes of the lines yield the values of k_{Cr} listed in Table I. Considering that the individual values of k_{corr} represent a difference between two comparable numbers, the precision of the values of k_{Cr} is probably not better than ~(15–20)%.

Reactions of radicals with $Co([14]aneN_4)(H_2O)_2^{2+}$ (eq 12) are the reverse of photohomolysis processes used to generate the radicals. The kinetic measurements and data treatment were

$$R^\bullet + Co([14]aneN_4)(H_2O)_2^{2+} \xrightarrow{k_{Co}} RCo([14]aneN_4)(H_2O)^{2+} + H_2O \tag{12}$$

analogous to those described for Cr^{2+}, i.e. $k_{obsd} = k_0[R^\bullet] + k_{MV}[MV^+] + k_{Co}[Co([14]aneN_4)(H_2O)_2^{2+}]$. The rate constants were determined for only two radicals, methyl and ethyl. The

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reactions are slow compared to the competing reactions of MV^+ (Table I). This required the use of large amounts (0.6–5 mM) of the highly air-sensitive cobalt(II) complex. Even minute concentrations of $Co([14]aneN_4)(H_2O)_2^{3+}$ or the peroxocobalt species in the stock solutions of $Co([14]aneN_4)(H_2O)_2^{2+}$ were sufficient to destroy most or all of the MV^+ present in the cell at much lower concentrations, typically $<5 \times 10^{-5}$ M. Owing to these experimental difficulties, the scatter of the data is large. A standard deviation of 30% is considered realistic for the two rate constants.

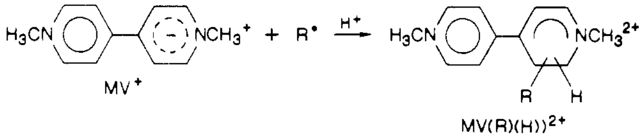
Discussion

The photolysis by visible light of the complexes $RCo([14]aneN_4)(H_2O)^{2+}$ results in the homolysis of the cobalt–carbon bond as the only process. This has been confirmed and documented by a number of independent qualitative and quantitative observations in this work as well as in the work on the methyl derivative reported earlier.[21]

The photochemical reaction of eq 7 produces equimolar amounts of the radicals and $Co([14]aneN_4)(H_2O)_2^{2+}$. The latter is a stable species, and it accumulates in the solution. The interference from the reverse of reaction 7 is, however, not a problem owing to the low value of the rate constant k_{Co} relative to the rate constants for the self-reactions of the radicals.[28]

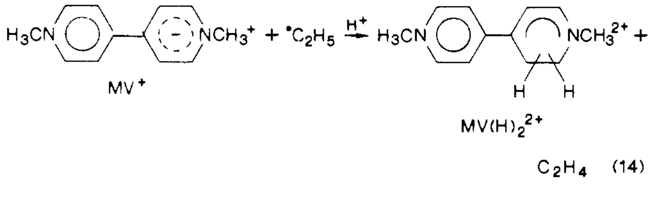
The organocobalt complexes described in this work are chemically quite unreactive toward a large variety of reagents. This property is crucial if these complexes are to be used as radical precursors in the presence of a variety of potential reagents. In addition to the low reactivity toward the dealkylating agents, these complexes are also unreactive toward such strong reductants as Cr^{2+} and MV^+ and can be oxidized only by very strong oxidants such as $Ru(bpy)_3^{3+}$.[29] Even that reaction is quite slow for the methyl, chloromethyl, and bromomethyl complexes. The results of the cyclic voltammetry on the methyl complex[21b] in CH_3CN suggest that the one-electron reduction and the one-electron oxidation of the complex take place at −0.78 and >+1.4 V vs SCE, respectively.

The reactions of the alkyl radicals listed in Table I with methyl viologen radical cation are all quite rapid, $k_{MV} = (1–2) \times 10^9$ M^{-1} s^{-1}. The major products of the reactions of $^{\bullet}CH_3$ and $^{\bullet}C_2H_5$ are not gaseous, which rules out electron transfer as a significant pathway. Although the products have not been identified, it is almost certain that addition of $R^{\bullet}$ to MV^+ takes place. One possibility[26] is shown in eq 13. The species $MV(R)(H)^{2+}$ can be pictured as a product of addition of RH to one of the double bonds of the aromatic system of MV^{2+}.



(13)

The methyl radical apparently reacts exclusively by this or some closely related pathway. The extra ethylene found among the products of the reaction of MV^+ and $^{\bullet}C_2H_5$ indicates that reaction 14 takes place in addition to the dominant path of eq 13. These two reactions represent a somewhat unusual case of radical cross-disproportionation and cross-combination, respectively. It would appear that both reactions initially yield a deprotonated methyl viologen product, which then reacts with a hydrogen ion to give the stable $MV(H)_2^{2+}$ or $MV(R)(H)^{2+}$. The lack of any acid dependence on the reactivity of MV^+ toward the radicals in the pH range 1–7 rules out the protonation prior to or during the rate-determining step.



(14)

The combination of the high reactivity of MV^+ toward the alkyl radicals and the large absorbance changes around 600 nm associated with these reactions makes MV^+ quite suitable as a probe[1f,20] in the determinations of the rate constants for the reactions of radicals with reductants. The study of the reactions of Cr^{2+} thus had a dual purpose: to "calibrate" the method against the reported rate constant for the reaction of the methyl radical[30a] and to measure the unknown rate constants for other radicals. The kinetics of the reactions of Cr^{2+} with a number of functionalized carbon-centered radicals have been studied by pulse radiolysis,[30] but no data are available for the hydrocarbon radicals with the exception of the methyl. All the reported rate constants fall in a narrow range, $(0.3–2) \times 10^8$ M^{-1} s^{-1}. As expected, sterically crowded radicals react more slowly. The rate constant for the reaction with the methyl radical obtained in this work, 2.2×10^8 M^{-1} s^{-1}, is in excellent agreement with the reported value of 2.4×10^8 M^{-1} s^{-1}, especially in view of the large standard deviations (15–20% in both cases). The agreement between the two values, as well as the reasonableness of the rate constants for the other radicals in Table I, lends strong support to the validity of our method.

The surprising result is the low reactivity of $Co([14]aneN_4)(H_2O)_2^{2+}$ toward the radicals. The two rate constants in Table I are among the lowest reported for a cobalt(II)–radical reaction that results in the formation of the cobalt–carbon bond. Admittedly, the reports on such reactions are quite scarce,[8b,31–35] and this is the first one on cobalt(II) complexes containing only saturated ligands. The kinetics of these reactions are probably controlled by the rates of water substitution at the cobalt center. This view is supported by the fact that the inner-sphere reaction of $Co([14]aneN_4)(H_2O)_2^{2+}$ with O_2 takes place with a rate constant of 1.2×10^7 M^{-1} s^{-1},[36] which is within the error identical with those measured for the methyl and ethyl radicals. This is consistent with all three reactions taking place by a dissociative process, although the data are not sufficient to distinguish between a D and an I_d mechanism. We are presently investigating reactions of other macrocyclic cobalt(II) complexes with carbon-centered radicals, in order to sort out the effects of the macrocyclic ligands on the kinetics and thermodynamics of the Co–C bond.

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Registry No. MV^+, 25239-55-8; $Co([14]aneN_4)(H_2O)_2^{2+}$, 65554-13-4; $CH_3Co([14]aneN_4)(H_2O)^{2+}$, 51240-12-1; $C_2H_5Co([14]aneN_4)(H_2O)^{2+}$, 111323-55-8; $C_3H_7Co([14]aneN_4)(H_2O)^{2+}$, 111323-58-1; $ClCH_2Co([14]aneN_4)(H_2O)^{2+}$, 111323-60-5; $BrCH_2Co([14]aneN_4)(H_2O)^{2+}$, 111323-62-7; $CH_3OCH_2Co([14]aneN_4)(H_2O)^{2+}$, 111323-64-9; $^{\bullet}CH_3$, 2229-07-4; $^{\bullet}C_2H_5$, 2025-56-1; $^{\bullet}C_3H_7$, 2143-61-5; $^{\bullet}CH_2OCH_3$, 16520-04-0; $^{\bullet}CH_2Cl$, 6806-86-6; $^{\bullet}CH_2Br$, 16519-97-4; Cr^{2+}, 22541-79-3.

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