decreases observed here ensure that the ensemble of reactant ions is well sampled. Our initial results indicate that the collisional cooling of vibrationally hot ions may be a surprisingly inefficient process requiring on the order of 100 collisions.

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(10) During an experiment, thermal electrons are continuously removed by trapping plate ejection. F^- ion is routinely ejected by a double resonance pulse turned on simultaneously with the laser pulse. If F^- is not ejected, a transient decrease is observed followed by a full recovery of the initial CH_3OHF^- signal amplitude. This occurs since photochemically formed F^- reacts with methyl formate via eq 2 to regenerate CH_3OHF^-

(11) Estimated using quantum-RRK theory. See Robinson, P. J.; Holbrook, K. A. "Theory of Unimolecular Reactions"; Academic Press: New York, 1972.

(12) Calculated assuming $\ln (I/I_0) = -\sigma F$ where I/I_0 is the ratio of signal heights with and without the laser and F is the number of photons per unit area. We anticipate that this will be a valid approximation in the limit where photodissociation is extensive.

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Early Events and Transient Chemistry in the Photohomolysis of Alkylcobalamins[1]

Sir:

Photoinduced metal-ligand homolysis is well established as a characteristic kind of reaction of transition metal complexes.[2,3] However, many features of such reactions have continued to be controverisal despite extensive investigations. Major points at issue have been the elucidation of the roles of geminate radicals trapped by a solvent cage and their excited state precursors.

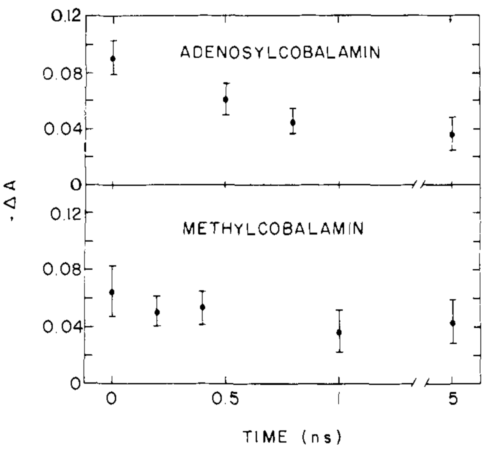

Figure 1. Time dependence of the substrate bleaching at 565 nm for both compounds studied. See ref 18 for experimental details.

Photochemical studies of complexes of cobalt have been relatively extensive and have been the basis of most of the discussions of photohomolysis in transition metal complexes.[2,3] The observed photochemical behavior[4-9] may be most simply described by the sequence of events: (1) absorption of radiation produces a Franck-Condon excited state (Y*), which (2) rapidly loses its excess vibrational energy ($k_v > 10^{11}$ s^{-1}) to form the thermalized excited state Y_0, followed by (3) product formation and internal conversion to the ground state from Y_0. At present, little can be said about whether or not additional excited states mediate product formation. Models which attribute all the details of variations of ϕ_R and product distributions to the behavior of radical pair species[2d,e] seem less in accord with observations.[2b,3] Heretofore, there have been no direct observations on the behavior of excited state or radical-pair precursors to the homolysis products in transition metal systems.

Photohomolyses of organocobalt complexes are qualitatively similar to the patterns noted above.[9-12] The biological functioning of adenosylcobalamin (coenzyme B_{12}) is very often described in terms of thermal Co-L homolysis and complex free-radical reactions in the enzymatic environment.[13] Photohomolyses of organocobalamines or organocobaloximes are often studied to elucidate the chemistry of appropriate intermediate species.[14] Recently, in such a study of homolysis of adenosylcobalamin in aqueous propane-1,2-diol, Lowe and co-workers[15] found a several-fold increase in the cobalt (II) EPR signal when the irradiated frozen solutions were warmed; this was interpreted as indicating a precursor to the homolysis step and parallels were drawn to the free-radical mechanism proposed for function of the coenzyme.[13] However, a long-lived precursor stands in contrast to the interpretation of photohomolysis patterns[2b,3] outlined above.

In this paper we report our studies of the transient intermediates generated following irradiations of methyl- and adenosylcobalamin. For the study of primary homolysis fragments, we used a picosecond flash photolysis technique[16] employing 3-4-mJ, 527-nm pulses of ~6 ps duration and a visible continuum probe beam generated by pulsing CCl_4 with the 1054-nm laser fundamental.[17,18] These experiments were performed in aqueous solutions, approximately millimolar in the organocobalamin with 2-mm path length cells. The photolysis cross section was about 4.5 mm^2. Flash photolyses of aerated or deaerated aqueous and ~90% 2-propanol (~10% water) solutions were performed using techniques described previously.[3,11] The cobalamin substrates were obtained from Sigma Chemical Co. and solutions and compounds were handled in darkened rooms. Fresh samples were substituted after about 25 laser shots. No more than a few percent change in the photolyzed samples' absorbancy was noted under these conditions.

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Table I. Kinetic Parameters Obtained in Picosecond Photolyses of Alkylcobalamins

	methylcobalamin	adenosylcobalamin
ΔA_∞ (474 nm)[a]	0.035 ± 0.006	0.016 ± 0.004
ΔA_0 (474 nm)[b]	0.060 ± 0.012	0.057 ± 0.017
ϕ_p[c]	0.33 ± 0.12	0.39 ± 0.12
ϕ_R (lit.)[d]	0.19	0.11
ϕ_R (calcd)[e]	0.16 ± 0.05	0.09 ± 0.035
$10^{-9}\,k_{\text{cage}}$, s^{-1} [f]	*g*	1.8 ± 1.0
$10^{-9}\,k_r$, s^{-1} [h]	*g,i*	1.3 ± 1.1
$10^{-9}\,k_d$, s^{-1} [h]	*g,i*	0.5 ± 0.4

[a] Absorbance change 5 ns after pulse. [b] Absorbance change 0 to 5 ps after pulse. [c] Based on $\Delta A_\infty/\Delta A_0$ and ϕ (lit.)[d] $\propto \Delta A_\infty$. [d] Reference 10. [e] Based on ΔA_∞. The bleaching in the sample region traversed by the probe beam has been estimated to be 57% based on work with $Fe(bipy)_3^{2+}$ (see Creutz et al., ref 16b). [f] Based on first-order kinetic treatment of absorbance decay at 474 nm *and* absorbance increase at 565 nm (i.e., $\ln|\Delta A - \Delta A_\infty| = \text{constant} + k_{\text{cage}}t$). [g] The absorbance differences, $\Delta A - \Delta A_\infty$, were too small compared to the estimated error limits to permit a reliable estimate of k_{cage} (see also Figure 1). [h] Based on $\phi_R = \phi_p[k_d/(k_d + k_r)]$ and $k_{\text{cage}} = k_d + k_r$. [i] If k_r were ~1×10^9 s^{-1} for both the methyl and adenosyl radicals, k_d would be ~1.4×10^9 s^{-1} for the methyl radical.

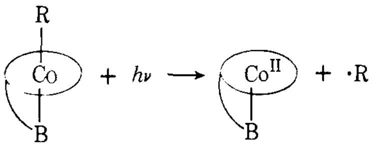
The 527-nm, picosecond excitations of methyl- and adenosylcobalamin resulted in transient absorbance changes in the visible spectral region (see Figure 1). For both compounds we found a "prompt" (≤8 ps) substrate bleaching in the 565-nm region and a correspondingly increased 474-nm absorbance attributable to cob(II)alamin.[19] Over a period of several hundred picoseconds there was a subsequent bleaching of the 474-nm absorbance and a corresponding increase in the 565-nm absorbance. The constant absorbancies observed after ~1 ns were smaller than those of the substrate before photolysis at 565 nm, but greater at 474 nm. As noted in Table I, "final" absorbance changes at ~1 ns were in excellent agreement with the quantum yields of Taylor et al.,[10] where these investigators based their yields on continuous photolyses and total oxygen scavenging of the alkyl radicals produced in homolysis.

We did not find any very short time absorbance changes that could be associated with long-lived excited states of the substrate (excited-state lifetimes were ≤8 ps). By extrapolation of the transient absorbance changes, we were able to estimate that the primary yield, of cage-trapped cob(II)alamin and R·, was $\phi_p \simeq 0.36$ for both compounds.

Two important points are to be stressed: (1) ϕ_p is only about 0.36 well into the plateau region of ϕ_R for both complexes; and (2) a very rapid radical-cobalt(II) recombination process is observed for excitations in the plateau region of ϕ_R (slower, bulk solution radical-cobalt(II) recombination reactions would occur on a microsecond time scale; see below and ref 11a). These observations indicate very rapid thermalization of the states populated by absorption ($k_v > 10^{11}$ s^{-1}) and are consistent with similar inferences based on the nearly wavelength independent quantum yields.

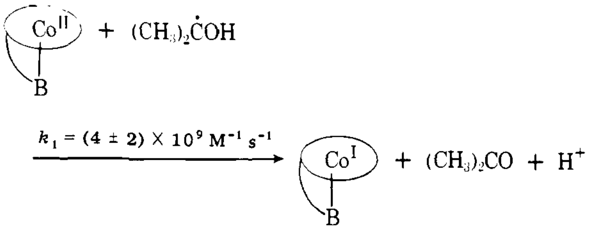
Our observations (Table I and Figure 1) indicate that the rates of disappearance of the cage-trapped products are probably similar for methyl- and adenosylcobalamin. One would expect the larger adenosyl radicals to diffuse more slowly than methyl radicals into bulk solution. However, the small signal to noise ratio for the methylcobalamin data precludes a quantitative comparison of these diffusion rates. Hopefully, future laser systems with more rapid firing rates will be able to improve the signal to noise ratios in these types of experiments.

Since there was no evidence for long-lived homolysis precursors in either methyl- or adenosylcobalamin, it seemed likely that the variations in the cobalt(II) signal found by Lowe et al.[15] could be due to secondary radical reactions. Consequently, we have examined the radical chemistry induced by flash photolytic irradiations of adenosylcobalamin. The behavior in aerated aqueous solution was not significantly different from that reported previously for methylcobalamin[11a]: formation of cob(II)alamin during the flash pulse (~40 μs), followed by rapid (k ~ 3×10^9 M^{-1} s^{-1}) alkylperoxy radical reaction with the cobalt(II) complex. In deaerated aqueous solution the 474-nm absorbance (cob(II)alamin) decayed only very slightly (~10%), presumably owing to radical-cobalt(II) reactions. Again complementary absorbance changes occurred at 530 nm, while at 386 nm there was a very small absorbance increase (ΔA ~ 0.008) during the flash pulse and slow (τ ~ 4 ms) absorbance decay. It seems likely that such small 386-nm absorbance changes are related to the chemistry of the adenosyl radical, although very small amounts of cob(I)alamin may be implicated. In deaerated 90% 2-propanol, the absorbance changes immediately following the flash pulse corresponded to decomposition of substrate (absorbance decrease at 530 nm) and formation of cob(II)alamin (absorbance increase at 474 nm). Over a period of ~400 μs, the 474-nm absorbance decreased to less than its value before the flash, then increased again over a period of ~0.2 s. The absorbance changes at 530 nm were similarly complex, but opposite in the direction of absorbance change and smaller in magnitude. A larger absorbance change (ΔA ~ 0.1; about twice that observed at 474 nm) was measured at 386 nm. At this shorter wavelength the absorbance increased over a period of ~400 μs and decreased over a period of ~0.2 s. The initial (~400 μs) absorbance changes are in a time scale characteristic of radical reactions and most likely involve the reduction of cob(II)alamin (absorbance maximum at 474 nm) to produce cob(I)alamin (absorbance maximum at 386 nm). Under these conditions, 2-propanol should efficiently scavenge the adenosyl radical producing the strongly reducing[20] 2-hydroxypropyl radical:



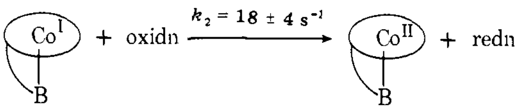
$$\cdot R + (CH_3)_2CHOH \rightarrow RH + (CH_3)_2\dot{C}OH \qquad (1)$$

Since the standard potential of the cob(II)alamin/cob(I)alamin couple is about −0.5 V against hydrogen,[21] eq 2 undoubtedly describes the reaction involved:[22-28]



(2)

The subsequent oxidation of cob(I)alamin



(3)

has not been fully characterized but could be the consequence of trace amounts of oxygen in solution or the formation and decomposition of hydridocobalamin species. Since radicals of the type RĊOH function as facile electron-transfer reagents,[2b,20] the generation of such radicals in the proximity of cob(II)alamin frequently leads to efficient formation of cob(I)alamin. Such a process readily accounts for the observations of Lowe and co-workers.[15] Such a process could be a complicating feature in the proposed radical mechanism for the function of dioldehydratases.

While the present study has involved organocobalt substrates, the general features are expected to be characteristic of photohomolysis in most transition metal complexes. More specifically, we can anticipate that, in those systems for which ϕ_R is a constant (significantly less than unity) over an appreciable range of excitation energies greater than E_{th}, there will be considerable excited-state thermalization and numerical values of ϕ_R will be a function of both excited-state dynamics and radical pair recombination statistics.

References and Notes

(1) The picosecond studies were carried out at Brookhaven National Laboratory under contract with the U.S. Department of Energy and supported by its Office of Basic Energy Sciences. The flash photolysis studies were carried out at Wayne State University. Partial support of this research by the National Institutes of Health is gratefully acknowledged.

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Flow Tube Measurement of the Rate Constants of the $N(^2D, ^2P, \text{and } ^4S) + Cl_2$ Reactions

Sir:

Love et al.[1] have recently published the first results of their crossed molecular beam experiments of atomic nitrogen plus halogen reactions. Their arc-heated (7000–15 000 K) nozzle beam source produces a mixture of $N(^4S, ^2D, \text{and } ^2P)$ species, which complicates the analysis of their reactive scattering data.

We present here the results of a brief kinetic study, at 298 K, of the $N(^2D) + Cl_2$, $N(^2P) + Cl_2$, and ground-state $N(^4S) + Cl_2$ reactions using the discharge-flow, resonance fluorescence method. The metastables are found to react very rapidly with Cl_2, i.e., $k_{^2D} = 3.6 \times 10^{-11}$ and $k_{^2P} = 2.2 \times 10^{-11}$ cm^3 s^{-1}. Their high detectability ($\gtrsim 10^9$ cm^{-3}) and low initial concentration ($\sim 10^{11-12}$ cm^{-3}) permits the unambiguous measurement of elementary rate constants. The reaction of ground-state N atoms is about four orders of magnitude slower, $k_{^4S} \simeq 2 \times 10^{-15}$ cm^3 s^{-1}, and, although this value is in qualitative agreement with two published results,[2,3] it lies near the lower limit of the measurable range accessible to this method.

The flow tube apparatus is a modification of an earlier one,[4] the principal difference being the use of resonance fluorescence rather than absorption which increases detection sensitivity by a factor of 10. This makes it possible to measure the kinetics of $N(^2P)$ whose initial concentration is smaller than that of $N(^2D)$ by about a factor of 6. A microwave discharge in flowing He + 1% N_2, which emits the strong multiplets at

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