reacts at −70 °C with magic acid–SO_2. Formation of a diacylium ion is ruled out since no appropriate increase of the water band was observed.[8] The aromatic protons of **2c** show a significant downfield shift compared with **1c** (Table I) and with diprotonated phthalimid; this may also rule out the formation of diprotonated phthalic anhydride **3**.[9]

An insight into system **2c**, is obtained from its ^{13}C NMR spectrum (Table I). The chemical shifts of the carbonyl carbons of **2c** show an intermediary value of the two carbonyl carbons of **2a** (δ ($COOH_2^+$) 178.1 ppm, δ(CO^+) 147.2 ppm, δ average 162.6 ppm, δ observed 164.7 ppm) (Table I). The ipso carbon atoms of **2c** appear at 118.6 ppm, the ipso carbon atoms of **2a** appear at 99.4 and 140.8 ppm, average 120.1 ppm (Table I). These data together with the disappearance of the OH^+ band and the downfield shift of the aromatic protons of **2c** are in agreement with the following conclusion: A fast migration (in the NMR scale) of a molecule of water occurs between the two adjacent carbonyls of **2c**. This fast rearrangement occurs either in the following process: **2c** $\rightleftharpoons$ **4** $\rightleftharpoons$ **5** $\rightleftharpoons$ **2c′**, a degenerate process, or by the formation of a single species, e.g., **6**. It seems that **6** need not show an averaging of the chemical shifts, of the ipso and the carbonyl carbon atoms and therefore the acylium–carboxonium rearrangement **2c** $\rightleftharpoons$ **2c′** is preferred.

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(8) Quenching experiments with methanol never gave any dimethyl phthalate; however, monomethyl phthalate is the main quenching product. A similar observation has also been made in the study of protonation of anhydrides.[2]
(9) Protonation of phthalimid which is isoelectronic to phthalic anhydride shows a similar chemical shift of the aromatic protons to **1c** and not to **2c**. Cf. G. A. Olah et al., *J. Am. Chem. Soc.*, **90,** 6464 (1968).

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Vestiges of the "Inverted Region" for Highly Exergonic Electron-Transfer Reactions

Sir:

The Marcus theory for outer-sphere electron-transfer reactions predicts that a plot of log k_{12} (k_{12}, the rate constant for the electron-transfer reaction) vs. $\Delta G°_{12}$ (the free energy change for the electron-transfer reaction) for constant reorganization energy should be parabolic. One remarkable feature of the theory is the so-called "inverted" region; when $-\Delta G°_{12} > 2(\Delta G^*_{11} + \Delta G^*_{22})$ where $(\Delta G^*_{11} + \Delta G^*_{22})/2$ is the intrinsic electron-transfer barrier, the reaction rate constant should *decrease* as the free energy change becomes more favorable. When k_{12} is calculated from eq 1[1]

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2} \qquad (1a)$$

$$\log f_{12} = \frac{(\log K_{12})^2}{4 \log \left(\frac{k_{11}k_{22}}{Z^2}\right)} \qquad (1b)$$

(where k_{11} and k_{22} are the self-exchange rates for the oxidizing and reducing couples, respectivel, K_{12} is the equilibrium constant for the cross-reaction, and Z is a collision number usually taken as 10^{11} M^{-1} s^{-1}), the point of crossover into the inverted region may be expressed as (eq 1c).

$$\log K_{12} = 2 \log (Z^2/k_{11}k_{22}) \qquad (1c)$$

It is apparent from condition 1c that crossover into the inverted region is favored when *both* K_{12} and $k_{11}k_{22}$ are large. Few opportunities for systematic exploration of the inverted region arise when both reactants are in their ground electronic states since K_{12} is not sufficiently large. On the other hand, excited state systems with small reorganization energies provide excellent probes of this region. Rehm and Weller sought evidence for inverted behavior in the electron-transfer quenching of hydrocarbon fluorescence. The quenching rate constants were, however, found to lie at the diffusion-controlled limit from $\Delta G°_{12} = -10$ to -62 kcal mol^{-1} even though onset of the inverted region is expected at $\Delta G°_{12} \sim -15$ kcal mol^{-1}.[2] In the present study we have used inorganic oxidants with small reorganization energies to quench the luminescence of polypyridineruthenium(II) complexes. For this series with $k_{11}k_{22} \sim 10^{16}$ M^{-2} s^{-2} ($\Delta G^*_{11} + \Delta G^*_{22} \sim 8$ kcal mol^{-1}) and $-\Delta G°_{12} = 10$ to 46 kcal mol^{-1} (inversion predicted at $-\Delta G°_{12} > 16$ kcal mol^{-1}), we do find evidence for diminished rate constants in the inverted region.

We have studied the quenching of the luminescence of the charge-transfer excited states of two polypyridineruthenium(II) complexes RuL_3^{2+} (L = 2,2′-bipyridine or 4,4′-dimethyl-2,2′-bipyridine) by trivalent polypyridine ML_3^{3+} complexes. Quenching rate constants k_q were obtained from lifetime measurements[3] in 0.5 M sulfuric acid at 25 °C in deaerated solutions. Quenching in these systems is ascribed to an electron-transfer process (eq 2)

$$^*RuL_3^{2+} + ML_3^{3+} \xrightarrow{k_q} RuL_3^{3+} + ML_3^{2+} \qquad (2)$$

in which the RuL_3^{2+} excited state, a very strong reducing agent (for L = bpy, $E^0 = -0.83$ V;[4] for L = 4,4′-$(CH_3)_2$bpy, $E^0 = -0.94$ V[3]), gives up an electron to the ML_3^{3+} complex (E^0 = −0.25, +0.82, +1.10, +1.26 V for $Cr(bpy)_3^{3+}$,[5] $Os(bpy)_3^{3+}$,[6] $Ru(4,4'\text{-}(CH_3)_2bpy)_3^{3+}$,[3] and $Ru(bpy)_3^{3+}$,[3] respectively). The quenching rate constants determined in this study are plotted against the driving force for electron-transfer quenching in Figure 1. For all seven systems studied the quenching rate constants lie near the diffusion-controlled limit which is (3–4) × 10^9 M^{-1} s^{-1} for reactants of this typeat 25 °C and 0.5 M ionic strength.[3,7] The first three points show a small increase in rate constant as K_{12} for electron-transfer quenching increases. At larger K_{12} values, however, the rate constants *decrease* with increasing driving force. The behavior observed in Figure 1 is thus in qualitative agreement with the predictions of Marcus theory.

We now examine in greater detail the evidence for this conclusion. Bolletta et al. demonstrated that $Cr(bpy)_3^{3+}$ quenching of $^*Ru(bpy)_3^{2+}$ does not proceed by an energy-transfer process[8] and Ballardini et al. have used a flash-photolysis technique to detect the electron-transfer products, $Cr(bpy)_3^{2+}$ and $Ru(bpy)_3^{3+}$, formed from quenching according to eq 2.[9] Thus this electron-transfer quenching mechanism is firmly established for the $Cr(bpy)_3^{3+}$/$^*Ru(bpy)_3^{2+}$ (and, by analogy, for the $Cr(bpy)_3^{3+}$/$^*Ru(4,4'\text{-}(CH_3)_2bpy)_3^{2+}$) system. Next, the self-exchange rates for the ML_3^{3+} oxidants used are very similar: for the $Cr(bpy)_3^{3+}/Cr(bpy)_3^{2+}$ couple $k_{11} \sim 10^8$ M^{-1} s^{-1} at 25 °C

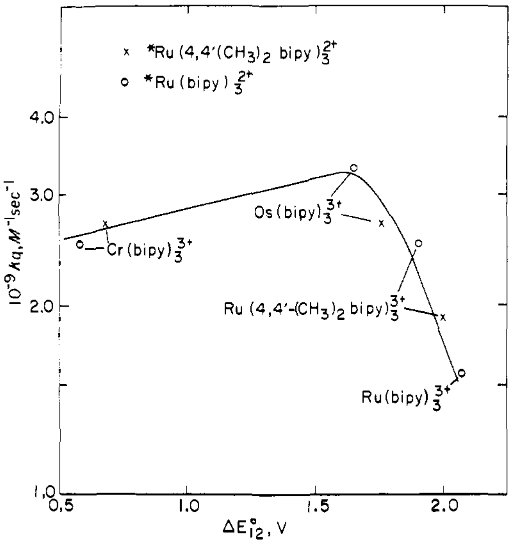

Figure 1. Plot of the logarithm of k_q, the quenching rate constant (25 °C, 0.5 M H_2SO_4), vs. $\Delta E^0{}_{12}$, the driving force for electron-transfer quenching. The reduction of the osmium(III) and ruthenium(III) complexes by water presents no problems under these conditions; for $Ru(bpy)_3{}^{3+}$ (the least stable of the complexes used here) the half-life for reduction to $Ru(bpy)_3{}^{2+}$ is ~7.5 h in 0.5 M sulfuric acid at 25 °C. As each set of τ measurements takes less than 0.5 h, the thermal decomposition has a negligible effect on the k_q values obtained from the lifetime quenching measurements. Furthermore it is unlikely that photodecomposition of the quenchers is important since the lifetime values for freshly and repetitively flashed solutions agreed to 2-4%. The uncertainty for the k_q values is estimated to be ±5%.

is estimated from cross-reaction rate constants,[10] while for $Os(bpy)_3{}^{3+}/Os(bpy)_3{}^{2+}$ and the $RuL_3{}^{3+}/RuL_3{}^{2+}$ couples k_{11} values have been found to be $\sim 10^8$ M^{-1} s^{-1} at 25 °C.[11] Thus the rate constant decrease observed is not an artifact arising from larger reorganization energies for the ruthenium(III) and osmium(III) oxidants. It is noteworthy that the two lowest k_q values shown in Figure 1 are associated with reactants for which excited-state self exchange (eq 3) may occur in parallel with quenching to give ground-state products (eq 4).

$$^*RuL_3{}^{2+} + RuL_3{}^{3+} \rightleftharpoons RuL_3{}^{3+} + {}^*RuL_3{}^{2+} \qquad (3)$$

$$^*RuL_3{}^{2+} + RuL_3{}^{3+} \rightarrow RuL_3{}^{3+} + RuL_3{}^{2+} \qquad (4)$$

The occurrence of process 3 could, however, result in a net lowering of the rate constant for reaction 4 only if (a) there is very strong interaction between $^*RuL_3{}^{2+}$ and $RuL_3{}^{3+}$ (exciplex formation) or (b) if reactions 3 and 4 proceed via a common activated complex. Otherwise the self-exchange process has a negligible effect; exchange of an electron between $^*RuL_3{}^{2+}$ and $RuL_3{}^{3+}$ simply regenerates the starting reactant pair and does not diminish the probability of reaction 4. The latter situation is shown in Figure 2 which depicts the potential energy surfaces as a function of nuclear coordinate for self-exchange and quenching (eq 3 and 4).[12]

Finally, it could be argued that the Os(III) and Ru(III) quenchers exhibit a discontinuity on this kind of plot because quenching occurs by another mechanism entirely in these systems (for example, for the $RuL_3{}^{3+}$ ions, via energy transfer to the LMCT excited states corresponding to the 675and 638 nm absorption maxima). However, to the extent that non-electron-transfer quenching mechanisms are operative, the case for inverted behavior in the electron-transfer quenching is only strengthened; if the k_q value plotted in Figure 1 is a composite rate constant for two (or more) quenching processes, the electron-transfer quenching constant must be even smaller. Thus the conclusion that inverted behavior is being observed is inescapable. Furthermore this is as expected from condition 1c: The $^*RuL_3{}^{2+}/RuL_3{}^{3+}$ self-exchange k_{22} is $\geq 10^7$ M^{-1} s^{-1}.[3] For the $Cr(bpy)_3{}^{3+}$ quenching log K_{12} is ~10, the right-hand side of eq 1c is ≤ 14 and these systems are at the "threshold" of the inverted region. The remaining systems thus lie far into the inverted region since log K_{12} increases to 25-34 while the self-exchange rates remain constant.

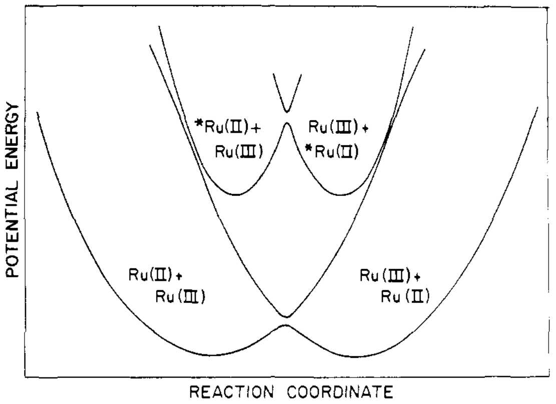

Figure 2. Cross-sections of the reactant and product potential energy surfaces. The upper pair of curves are for the self-exchange involving the excited ruthenium(II) complex (eq 3). The lower set of curves are for the ground-state self-exchange between $RuL_3{}^{2+}$ and $RuL_3{}^{3+}$ (eq 5). See footnote 12.

Since the rate constants in the inverted region (though low) are many orders of magnitude above those predicted from eq 1, the mechanism of the transition from excited-state reactant to ground-state product curves cannot involve a classical passage of the system *over* the "barrier"; that is, the reactions are not electronically adiabatic. This is also true for the Rehm and Weller systems. Consequently quantum mechanical mechanisms of barrier penetration have been invoked[13-16] to account for the results of Rehm and Weller. The mechanism of Efrima and Bixon[13] involves nuclear tunneling of the reactants to vibrationally excited states of the products, and these authors have shown semiquantitatively that this may be a feasible electron-transfer mechanism for relatively large molecules. The same mechanism could be operative in the $^*RuL_3{}^{2+}/RuL_3{}^{3+}$ reactions as well,[17] but, in this case, the increasing inefficiency of nuclear tunneling (poorer vibrational overlap) as the exergonicity of the reaction increases is actually observable in the rate constants. The behavior of the present system is thus closer than that of the Rehm and Weller systems to the predictions of current theories which feature diminished tunneling efficiencies at large $-\Delta G^\circ{}_{12}$.[14,16] Clearly further studies of highly exergonic reactions (probably through excited-state reactions)[18] will be required if the mechanisms of electron transfer in the inverted region are to be understood.

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to be 1.1×10^8 M^{-1} s^{-1} from a relative Marcus calculation using the $Cr(bpy)_3{}^{2+}/Co(NH_3)_6{}^{3+}$ and $Ru(NH_3)_6{}^{2+}/Co(NH_3)_6{}^{3+}$ cross-reactions (ref 10b and 10c) and 4×10^3 M^{-1} s^{-1} for the $Ru(NH_3)_6{}^{2+}/Ru(NH_3)_6{}^{3+}$ self-exchange rate constant (ref 10d), 3.5×10^8 M^{-1} s^{-1} from a relative Marcus calculation using the $Cr(bpy)_3{}^{2+}/Co(NH_3)_6{}^{3+}$ and $V^{2+}/Co(NH_3)_6{}^{3+}$ (ref 10e) cross-reactions with 1.0×10^{-2} M^{-1} s^{-1} for the V^{2+}/V^{3+} self-exchange (ref 10f), and 10^7 M^{-1} s^{-1} from the $Cr(bpy)_3{}^{3+}/V^{2+}$ cross-reaction for which $k = 4.2 \times 10^2$ M^{-1} s^{-1} at 25 °C and $\mu = 1.0$ M ($ClO_4{}^-$) (ref 10g). The E^0 values used for the Cr, Ru, and V couples are -0.25,[5] $+0.051$ (ref 10d), and -0.255 (ref 10h), respectively. (b) A. Zwickel and H. Taube, *Discuss. Faraday Soc.*, **29**, 42 (1960). (c) J. F. Endicott and H. Taube, *J. Am. Chem. Soc.*, **86**, 1686 (1964). (d) T. J. Meyer and H. Taube, *Inorg. Chem.*, **7**, 2369 (1968). (e) A. Zwickel and H. Taube, *J. Am. Chem. Soc.*, **83**, 793 (1961). (f) K. V. Krishnamurty and A. C. Wahl, *J. Am. Chem. Soc.*, **80**, 5921 (1958). (g) M. Chou, unpublished observations, Brookhaven National Laboratory, 1976. (h) W. M. Latimer, "Oxidation Potentials", 2d ed, Prentice-Hall, Englewood Cliffs, N.J., 1952.

(11) For the $Fe(phen)_3{}^{3+,2+}$ exchange k_{11} has been reported to be 3×10^8 M^{-1} s^{-1} in aqueous 1.84 M sodium sulfate at 25 °C (I. Ruff and M. Zimonyi, *Electrochim. Acta*, **18**, 515 (1973)). M. Chan (M. Chan, Ph.D. Thesis, Washington University, 1974) has found k_{11} for $Ru(bpy)_3{}^{3+,2+}$ to be ~1.5 times that for $Fe(phen)_3{}^{3+,2+}$ and k_{11} for $Os(bpy)_3{}^{3+,2+}$ to be four times that for $Fe(phen)_3{}^{3+,2+}$ ($k_{11} = 6 \times 10^6$ M^{-1} s^{-1}) in acetonitrile at $\mu \sim 0.1$ M and 25 °C. Thus $k_{11} \geqslant 10^8$ M^{-1} s^{-1} in aqueous solutions at 0.5 M ionic strength seems a reasonable value for the $Os(bpy)_3{}^{3+,2+}$ and $RuL_3{}^{3+,2+}$ systems, allowing that self-exchange may be somewhat faster for Os(III) than Ru(III).

(12) Figure 2 depicts cross-sections of the reactant and product potential energy surfaces in the vicinity of the intersection region relevant to electron-transfer quenching of $^*RuL_3{}^{2+}$ by $RuL_3{}^{3+}$. The upper pair of intersecting curves are for self-exchange involving the excited ruthenium(II) complex (eq 3), while the lower set of intersecting curves are for the ground-state self-exchange (eq 5).

$$RuL_3{}^{2+} + RuL_3{}^{3+} \rightleftharpoons RuL_3{}^{3+} + RuL_3{}^{2+} \qquad (5)$$

Because quenching according to eq 4 lies in the inverted region, the intersection of the excited-state reactant curve with the ground-state product curve occurs on the left-hand side of the excited-state reactant curve; similarly the intersection of the excited-state product curve with the ground-state reactant curve occurs on the right-hand side of the excited-state product curve. Focusing on the excited-state reactant curve, in order for electron-transfer quenching to occur it is necessary that the system move to the left-hand side where nonadiabatic electron-transfer forming the electronic ground-state species can occur. If, on the other hand, the system moves to the right there is no net change aside from excited-state self-exchange, but, by symmetry, once excited-state self-exchange has occurred, crossing to the "reactant" ground-state curve may occur if the system moves again to the right. Thus the excited-state exchange reaction has no effect on quenching via crossing to the ground-state surfaces since this crossing is equally probably from either of the upper intersecting curves, and the excited-state exchange reaction does not waste time or motion that would otherwise lead to quenching.

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(17) Of course, electron transfer to produce electronically excited $RuL_3{}^{3+}$ or $ML_3{}^{2+}$ may offer another and distinctly different route leading eventually to ground-state $RuL_3{}^{2+}$ and $ML_3{}^{3+}$.

(18) Considerably more striking evidence for inverted behavior in systems of this kind is provided by the reaction

$$2\,^*Ru(bpy)_3{}^{2+} \rightarrow Ru(bpy)_3{}^{+} + Ru(bpy)_3{}^{3+} \qquad (6)$$

Preliminary flash-photolysis experiments in which the emission or solution absorbance was monitored at $^*Ru(bpy)_3{}^{2+}$ levels $>10^{-3}$ M indicate an upper limit of 10^7 M^{-1} s^{-1} (25 °C, $\mu = 0.5$ M) for the rate constant for reaction 6. Since the reorganization energies for the $^*Ru(bpy)_3{}^{2+}/Ru(bpy)_3{}^{+}$ and $^*Ru(bpy)_3{}^{2+}/Ru(bpy)_3{}^{3+}$ couples are small ($k_{11}k_{22} \sim 10^{14}$–$10^{18}$ M^{-2} s^{-2}, ref 3 and H. E. Toma and C. Creutz, *Inorg. Chem.*, in press) and $\Delta E^0{}_{12}$ is 1.7 V, the very small value obtained for this rate constant suggests that the $^*Ru(bpy)_3{}^{2+}$ disproportionation also manifests "inverted" behavior.

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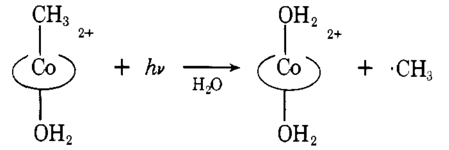
A Flash Photolytic Investigation of Low Energy Homolytic Processes in Methylcobalamin[1]

Sir:

Coordination complexes containing alkyl-cobalt bonds have been the subject of much interest since the discovery of coenzyme B_{12}.[2] The nature of the cobalt-carbon bond is a fundamental concern, both from the point of view of basic chemistry and as an aid in understanding the functioning of the coenzyme in protein substrates. The photochemistry of coenzyme B_{12} and related organocobalt complexes has been of continuing[3-10] interest, no doubt because the susceptibility of these systems to photoinduced homolytic processes has seemed qualitatively pertinent to the nature of the cobalt-carbon bond. In fact the photochemically determined threshold energies for homolytic processes (M–X → M + ·X) can be used as measures of M–X bond strength.[10] We report here some pertinent, direct observations of homolytic processes in methylcobalamin and related compounds.

We have recently shown that cobalt-methyl homolysis (eq 1) occurs following relatively low energy irradiations of complexes containing synthetic equatorial (N_4) ligands.[11,12]



$$CH_3\text{–}Co\text{–}OH_2{}^{2+} + h\nu \xrightarrow{H_2O} H_2O\text{–}Co\text{–}OH_2{}^{2+} + \cdot CH_3 \qquad (1)$$

For both $Co([14]aneN_4)(OH_2)CH_3{}^{2+}$ and $Co([14]tetraeneN_4)(OH_2)CH_3{}^{2+}$ the homolytic process (eq 1) occurs with large nearly wavelength independent quantum yields following monochromatic excitations in the visible absorption region.[11] A fairly well defined, low energy threshold (610 nm)[11b] for homolysis in $Co([14]tetraeneN_4)(OH_2)CH_3{}^{2+}$ implies that the cobalt–methyl bond energy is relatively small: about 47 kcal mol^{-1} assuming a bond of negligible polarity and similar energies of solvation for reactants and products.[10]

Our experience with homolysis in $Co^{III}L_5X$ systems[10,13] is that differences in Co–X homolysis energies vary with changes in the ligand field stabilization energy of the CoL_5 fragment, and solvation energies, but that the apparent Co–X bond energies are not otherwise greatly dependent on L. Thus we would predict that homolysis should occur for low energy irradiations of methylcobalamin, in accord with the observations of Taylor et al.[6] and of Pratt.[7b] More recently Hogenkamp et al.[5] have found that methylcobalamin is ". . . surprisingly resistant to . . . photolysis . . . ." in the absence of oxygen. Since the products of homolysis of $Co(N_4)(OH_2)CH_3{}^{2+}$ complexes have been established to recombine at rates apparently limited only by the rates of Co–OH_2 bond breaking,[14,15] and since the nonluminescent methylcobalamin excited states surely could not be sufficiently long lived to react directly with dissolved oxygen,[16-21] we have undertaken a flash photolysis study of methylcobalamin with a view to identifying and directly observing the reactions of any transient species.

A sample of purified, solid methylcobalamin was generously donated to us by Professor C. P. Dunne. Solutions approximately 6×10^{-6} M in methylcobalamin were prepared in water and in 2 M 2-propanol. A filter solution of $Ni([14]dieneN_4)^{2+}$ [22] and $FeCl_3$ in 1 M HCl was prepared concentrated enough to transmit only light with $\lambda > 480$ nm, and placed in a quartz jacket surrounding the sample cell. A stream of Cr^{2+} scrubbed nitrogen was passed through sample solutions for about 1 h when deaeration was necessary. All samples were handled in a darkened room and in shielded vessels. Standard flash photolysis techniques were employed.[23]

In all samples of methylcobalamin flash photolyzed we observed the efficient generation of B_{12r} during the flash pulse (Figure 1b). The amount of B_{12r}[24] generated was independent of medium conditions, i.e., we achieved about a micromolar yield of B_{12r} per 40×10^{-6}s, 160 J flash in water (aerated or deaerated) or 2-propanol (aerated or deaerated). The generation of B_{12r} was accompanied by a decrease in concentration of substrate (methylcobalamin). In deaerated aqueous solution the initial generation of B_{12r} was followed by a rapid partial decay which also corresponded to a rapid partial regeneration