TMPOR is the major product formed. The crucial experiment is that in entry 9. The major product of reaction of RBr with magnesium in the presence of *both* *t*-BuOH and TMPO· is TMPOR, even though entries 4 and 5 indicate that RMgBr, if formed, would react preferentially with the *t*-BuOH under these conditions and yield RH. We rationalize this observation by Scheme I, in which intermediate cyclopentyl radicals are trapped by TMPO· before they can be converted into cyclopentylmagnesium bromide.

We draw four conclusions from the data of Table I. First, reaction of RMgBr is faster with *t*-BuOH than with TMPO· (apparently by a factor of ~10). Second, when the reaction of RBr with magnesium is carried out in the presence of *t*-BuOH and TMPO·—conditions in which the Grignard reagent formed would be expected to be converted predominantly into RH—TMPOR is the major product observed. This observation is compatible with a mechanism (Scheme I) in which RBr is converted into R· on reaction with magnesium, and those radicals are trapped by reaction with TMPO· more rapidly than they are converted into RMgBr. Third, accepting Scheme I as a correct description of the mechanism of formation of TMPOR, the fact that the yield of TMPOR is >80% establishes that at least this fraction of the starting RBr is converted into radicals.[13] Fourth, the intermolecular trapping reported here,[14] the characteristic intramolecular rearrangements of 5-hexenyl,[3] and the CIDNP observed for Grignard products[4] are all compatible with free (as opposed to "surface-bound") alkyl radicals.[15]

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(10) We have not explicitly examined the mechanism of this reaction, but we assume it to be analogous to the electron-transfer process inferred earlier for the reaction of organolithium reagents with TMPO·: Newirth, T.; Whitesides, G. M. *J. Org. Chem.*, **1975**, *40*, 3448–3450. We do not know the rate constant for coupling TMPO· with cyclopentyl radicals, but the reaction of 2,2,6,6-tetramethyl-4-oxopiperidine-*N*-oxyl with cyclopentyl radical is ca. $k = 3.5 \times 10^8\ M^{-1}\ s^{-1}$: Nigam, S.; Asmus, K.-D.; Willson, R. L. *J. Chem. Soc., Faraday Trans. 1* **1976**, 2324–2340.
(11) TMPO· itself reacts at a clean magnesium surface under these conditions, but more slowly than cyclopentyl bromide (the latter rate is mass transport limited).[5]
(12) The yield of dimers and olefins is consistently higher in the reactions carried out in the presence of *t*-BuOH than in its absence. The greater importance of radical–radical reactions in systems containing *t*-BuOH *may* reflect a decrease in the rate of conversion of R· into RMgBr at the alkoxide-obscured magnesium surface.
(13) Similar studies with *n*-hexyl bromide have succeeded in trapping ~70% of the hexyl moieties as TMPO-*n*-hexyl.
(14) Bodewitz has described evidence indicating that methyl radicals produced in reaction of methyl iodide with magnesium are trapped by allyl phenyl ether: Bodewitz, H. W. H. J. Ph.D. Thesis, Der Vrije Universiteit, Amsterdam, 1975.
(15) A referee has suggested that TMPOR might be formed by reaction between surface-bound R· and TMPO·. It is difficult to prove or disprove this suggestion, since the differences between a hypothetical "surface-bound" radical and a free radical in solution have always been so vague as to frustrate experimental distinction. In the experiments reported here, any surface-bound radicals would have to have properties very similar to those of free radicals.

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Photochemical and Thermal Decomposition of $HCo(CO)_4$[1]. Evidence for a Radical Pathway Involving $Co_2(CO)_8$

Sir:

Hydridotetracarbonylcobalt(I), $HCo(CO)_4$, is presumed to be an active intermediate in several organic reactions catalyzed by cobalt carbonyl compounds. The mechanisms commonly written for these processes embody the well-known 16–18 electron rule.[2-4] However, evidence has accumulated in recent years that substitution, addition to olefins, oxidative addition, and electron-transfer processes may proceed through, or lead to, 17-electron radical species.[5-8] We report here upon a study of the thermal and photochemical decomposition reactions of $HCo(CO)_4$ in hexane solution:

$$2HCo(CO)_4 \rightarrow H_2 + Co_2(CO)_8 \qquad (1)$$

The results are consistent with a radical as opposed to an even-electron mechanistic scheme.

Hexane solutions of $HCo(CO)_4$ were prepared as described elsewhere.[9] The $HCo(CO)_4$ formed was condensed in hexane as solvent. The hexane solutions were vacuum distilled and stored in sealed tubes at liquid nitrogen temperature until used. Careful procedures result in solutions containing very little (but always some) $Co_2(CO)_8$. [Very small amounts of $HCo(CO)_4$ may decompose during distillation via a wall reaction.] Solutions with $HCo(CO)_4$ concentrations up to 0.1 M typically contain concentrations of $Co_2(CO)_8$ as low as 6×10^{-4} M, as estimated from IR absorbance values. However, solutions of even the lowest concentrations prepared exhibit absorbances $\gg 1$ at 366 nm with the path lengths employed in the photochemical studies.

Our observations regarding the thermal reaction are similar to those reported by others.[10,11] The rate has been described as second order in $HCo(CO)_4$. However, as noted by Clark et al.,[11] there is a dependence on $[Co_2(CO)_8]$; the initial rate of decomposition increased with increasing initial $Co_2(CO)_8$ concentration. In addition, we observe that a second-order plot for disappearance of $HCo(CO)_4$ is curved upward (Figure 1a), reflecting an increasing reaction rate as $Co_2(CO)_8$ is formed. This highly reproducible behavior is observed only when the initial $Co_2(CO)_8$ concentrations are low and the reaction is followed for ~2 half-lives or longer. We observe also, in

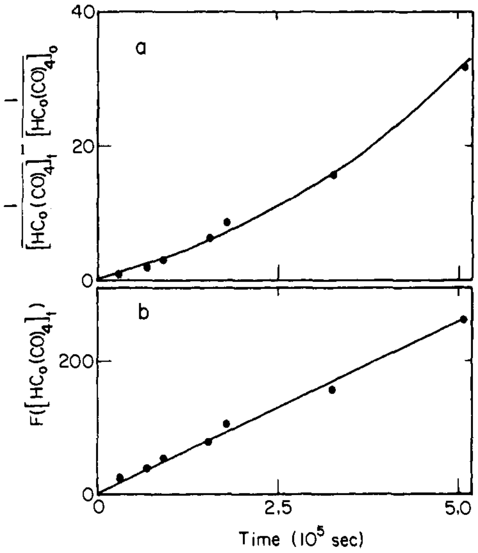

Figure 1. (a) A second-order plot for disappearance of $HCo(CO)_4$ in the thermal decomposition: $[HCo(CO)_4]_0 = 5.9 \times 10^{-1}$ M; $[Co_2(CO)_8]_0 \sim 1.3 \times 10^{-3}$ M. (b) Graph of rate data shown in part a, assuming that the rate of $HCo(CO)_4$ decomposition increases as $[Co_2(CO)_8]^{1/2}$ (eq 8).

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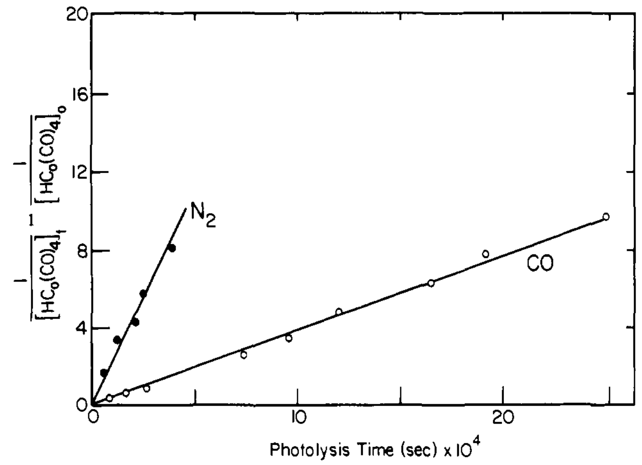

Figure 2. Second-order plot for disappearance of $HCo(CO)_4$ in the photochemical decomposition, under N_2 atmosphere and under 1 atm of CO.

agreement with previous work, that the reaction rate is inversely dependent on [CO].

The kinetics of the photochemical reaction have not been previously reported. Upon irradiation at 366 nm at room temperature decomposition is much faster than the thermal process. All of the absorbance at 366 nm is due to traces of $Co_2(CO)_8$; $HCo(CO)_4$ has negligible absorbance at this wavelength. Because absorption under the experimental conditions is essentially total, the rate of photodecomposition of $HCo(CO)_4$ is independent of added $Co_2(CO)_8$. The rate of photodecomposition is second order in $[HCo(CO)_4]$, and is inhibited by addition of CO at 1 atm (Figure 2).

Our results are not readily accounted for by a mechanistic scheme that involves CO loss from $HCo(CO)_4$ as a preequilibrium in the thermal reaction or primary photoprocess in the photochemical reaction. We propose the following mechanism:

$$Co_2(CO)_8 \rightleftarrows 2Co(CO)_4\cdot \quad (2)$$

$$Co(CO)_4\cdot \rightleftarrows Co(CO)_3 + CO \quad (3)$$

$$Co(CO)_3 + HCo(CO)_4 \rightleftarrows HCo_2(CO)_7\cdot \quad (4)$$

$$HCo_2(CO)_7\cdot + HCo(CO)_4 \rightarrow H_2Co_2(CO)_7 + Co(CO)_4\cdot \quad (5)$$

$$H_2Co_2(CO)_7 \rightarrow H_2 + Co_2(CO)_7 \quad (6)$$

$$Co_2(CO)_7 + CO \rightarrow Co_2(CO)_8 \quad (7)$$

The mechanism involves an initial formation of $Co(CO)_4\cdot$ radicals. The thermal reaction involves a homolytic preequilibrium; in the photochemical reaction, facile rupture of the Co-Co bond occurs via excitation of the σ-σ^* transition for $Co_2(CO)_8$. The labile $Co(CO)_4\cdot$ radicals lose CO;[8b,12] there follows an oxidative addition preequilibrium, a slower hydrogen atom transfer, and then reductive elimination of H_2. When the rate expression for the thermal reaction is integrated, recognizing that the reaction is autocatalytic in $Co_2(CO)_8$ via preequilibrium 2, one obtains

$$F([HCo(CO)_4]_t) = \frac{(K - \frac{1}{2}[HCo(CO)_4]_t)^{1/2}}{K[HCo(CO)_4]_t} + \frac{1}{4K^{3/2}} \log \frac{\{(K - \frac{1}{2}[HCo(CO)_4]_1)^{1/2} + K^{1/2}\}^2}{[HCo(CO)_4]_t} = kt \quad (8)$$

where $K = [Co_2(CO)_8]_0 + \frac{1}{2}[HCo(CO)_4]_0$. This function is displayed in Figure 1b for the same data shown in 1a. The fit is satisfactory through 2 half-lives.

The proposed mechanism leads to the following expression for the rate of $HCo(CO)_4$ loss in the photochemical decomposition:

$$-\frac{d[HCo(CO)_4]}{dt} = \frac{\kappa I_a[HCo(CO)_4]^2}{[CO]} \quad (9)$$

I_a represents the flux of photons, and κ is a collection of rate constants relating to equilibria 2-4 and rate-determining step 5. Although we have not tested the dependence of photochemical rate on I_a, we have observed the expected dependences on $[HCo(CO)_4]$ and [CO].

The commonly accepted mechanism for thermal decomposition or substitution of $HCo(CO)_4$ involves a presumed facile loss of CO to form $HCo(CO)_3$.[10,11] There is, however, little independent evidence that such a thermal process exists. The observation of rapid substitution of $HCo(CO)_4$ by a phosphine[13] is not supportive evidence, because such a substitution probably proceeds via a now well-established radical chain mechanism.[8,14] Compounds of the form $XCo(CO)_4$, where X = $Sn(C_6H_5)_3$, CF_3, and others, all undergo slow substitution at room temperature.[12,15] Only when X is a strongly cis-labilizing ligand such as -C(O)R[16] is substitution reasonably rapid at room temperature. Hydride is not expected to be a cis-labilizing ligand.[17,18]

Our present results thus strongly suggest a common radical mechanism for both the photochemical and thermal decomposition of $HCo(CO)_4$. These results also carry the implication that radical intermediates could be plausibly involved in much of the catalytic reaction chemistry involving $HCo(CO)_4$, $Co_2(CO)_8$, or related compounds.[19]

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Adamantyl Allenic Rhodopsin.
Leniency of the Ring Binding Site in Bovine Opsin

Sir:

We had previously shown[1] that bovine opsin not only binds to the 9-cis and 9,13-dicis isomers of 6,7-didehydro-5,6-dihydroretinal (**1**)[2] but is also capable of accepting all four diastereomers and enantiomers. In view of the high specificity usually encountered in binding sites, this lenient property of

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