

Thermodynamic and Activation Parameters for a (Porphyrinato)cobalt–Alkyl Bond Homolysis

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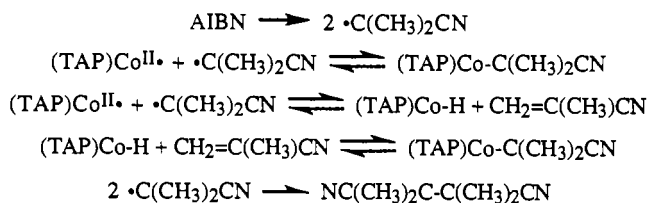
Received January 21, 1994^o

Equilibrium constant measurements for (TAP)Co–C(CH₃)₂CN dissociating into (TAP)Co^{II•} and •C(CH₃)₂CN provide a direct determination of the thermodynamic values for homolytic Co–C bond dissociation ($\Delta H^\circ = 18 \pm 1$ kcal mol⁻¹, $\Delta S^\circ = 23 \pm 2$ cal K⁻¹ mol⁻¹). Dissociation of (TAP)Co–C(CH₃)₂CN into the paramagnetic fragments ((TAP)Co^{II•}, •R) results in NMR line broadening that is used in deriving activation parameters related to the bond homolysis process ($\Delta H^\ddagger = 20 \pm 1$ kcal mol⁻¹, $\Delta S^\ddagger = 13 \pm 2$ cal K⁻¹ mol⁻¹). These studies provide the first examples where direct equilibrium constant measurements and NMR relaxation methods have been used in determining thermodynamic and activation parameters for an organo–metal homolysis reaction.

Introduction

Thermal cobalt–alkyl bond homolysis is an essential feature in the function of B₁₂ coenzyme,² cobalt (II)-catalyzed chain transfer in radical polymerization of alkenes,³ and organic substrate transformations⁴ where organocobalt(III) complexes function as intermediates. Studies directed toward evaluating Co–R bond homolysis enthalpies occupy a central position in the area of organo–transition metal energetics^{5,6} and contribute substantially to the understanding of the formation and reactivity of organocobalt(III) species. A few Co–R bond dissociation enthalpies have been determined by calorimetric⁷ and equilibrium measurements in conjunction with thermochemical cycles,⁸ but most studies have used kinetic methods^{5,6,9–11} that utilize chemical

Scheme 1



trapping of radicals produced in the bond homolysis. This article reports on equilibrium constant measurements and ¹H NMR exchange broadening studies for an organo(tetraanisylporphyrinato)cobalt complex, (TAP)Co–C(CH₃)₂CN, that yield thermodynamic values and activation parameters for the homolytic bond dissociation in solution. To our knowledge, these studies represent the first applications of these direct methods for obtaining thermodynamic and activation parameters for an organometallic (M–C) bond homolysis.

Results

Thermodynamic Values for the Homolytic Dissociation of (TAP)Co–C(CH₃)₂CN. (Tetraanisylporphyrinato)cobalt(II), (TAP)Co^{II•} (1) (5×10^{-3} M), in the presence of CH₂=C(CH₃)CN (0.14 M) reacts with •C(CH₃)₂CN (2) radicals from AIBN in chloroform solvent to form (TAP)Co–C(CH₃)₂CN (3) (Scheme 1, Figure 1). Reaction of (TAP)Co^{II•} with •C(CH₃)₂CN is known from chemical trapping studies to form (TAP)Co–H (4) in addition to 3. Excess methacrylonitrile (CH₂–C(CH₃)CN) is added to the reaction system to recycle (TAP)Co–H (4) as the alkyl complex 3 (Scheme 1). By prevention of the accumulation of 4, the termination of radicals through bimolecular reductive elimination of H₂ (2(TAP)Co–H → 2(TAP)Co• + H₂) is repressed such that bimolecular radical reactions that give coupling and disproportionation products are effectively the only radical termination mechanisms. For the specific case of •C(CH₃)₂CN, radical coupling is known to be the dominant mechanism.¹²

^o Abstract published in *Advance ACS Abstracts*, July 15, 1994.

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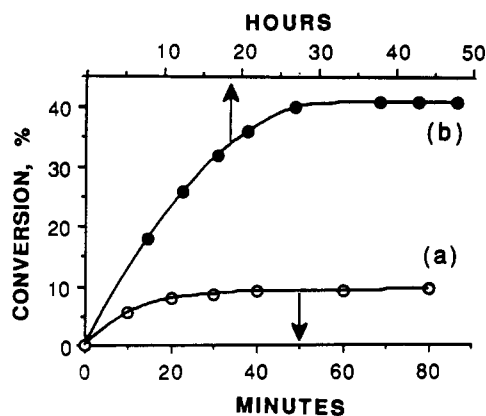
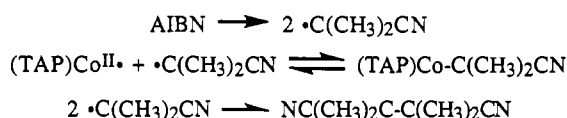


Figure 1. Percent conversion of $(\text{TAP})\text{Co}^{\text{II}*}$ to $(\text{TAP})\text{Co}-\text{C}(\text{CH}_3)_2\text{CN}$ in chloroform solvent as a function of reaction time and temperature $[\text{CH}_2=\text{C}(\text{CH}_3)\text{CN}] = 0.14 \text{ M}$; $[(\text{TAP})\text{Co}^{\text{II}*}]_i = 4.7 \times 10^{-3} \text{ M}$; (a) $[\text{AIBN}]_i = 0.08 \text{ M}$, $T = 333 \text{ K}$; (b) $[\text{VAZO-52}] = 0.08 \text{ M}$, $T = 296 \text{ K}$.

Scheme 2



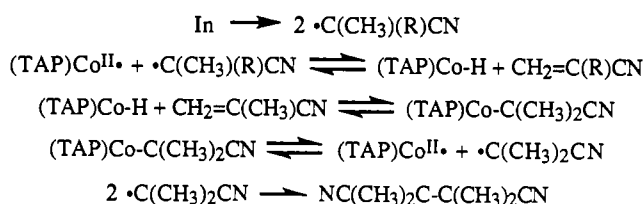
^1H NMR was used in monitoring the concentrations of solution species, and $(\text{TAP})\text{Co}^{\text{II}*}$ (**1**) and $(\text{TAP})\text{Co}-\text{C}(\text{CH}_3)_2\text{CN}$ (**3**) were the only species observed that contain the $(\text{TAP})\text{Co}$ unit. The actual reacting system contains intermediate radical pairs

$((\text{TAP})\text{Co}^{\text{II}*} \cdot \text{C}(\text{CH}_3)_2\text{CN})$ and $(\text{TAP})\text{Co}-\text{H}$ (**4**), but these species never attain ^1H NMR observable concentrations. An abbreviated reaction scheme that ignores these intermediates is adequate to describe the stoichiometry for this system (Scheme 2). The ratio of the concentration of $(\text{TAP})\text{Co}-\text{C}(\text{CH}_3)_2\text{CN}$ (**3**) to that of $(\text{TAP})\text{Co}^{\text{II}*}$ (**1**) is observed to increase with time as $\cdot \text{C}(\text{CH}_3)_2\text{CN}$ (**2**) is formed from AIBN and eventually achieves a constant steady state value (Figure 1). The initial concentrations of AIBN used in these studies were sufficiently large so that the rate of radical formation is effectively constant during the time required to achieve the steady state condition.

Steady state concentrations of $\cdot \text{C}(\text{CH}_3)_2\text{CN}$ radicals in solution were obtained from the rate at which radicals enter the solution ($V = k_i[\text{AIBN}]$) and the rate for radical termination ($2k_t[\text{R}\cdot]^2$) ($[\text{R}\cdot] = (V/2k_t)^{1/2}$). The concentration quotient for the homolytic Co-C bond homolysis of **3** ($(\text{TAP})\text{Co}-\text{C}(\text{CH}_3)_2\text{CN} \rightarrow (\text{TAP})\text{Co}^{\text{II}*} + \cdot \text{C}(\text{CH}_3)_2\text{CN}$) at steady state conditions corresponds to the equilibrium constant for bond homolysis ($K = [(\text{TAP})\text{Co}^{\text{II}*}][\cdot \text{C}(\text{CH}_3)_2\text{CN}]/[(\text{TAP})\text{Co}-\text{C}(\text{CH}_3)_2\text{CN}]$). Equilibrium constants evaluated by this procedure for a series of radical concentrations at a fixed temperature were found to be in substantial agreement (Table 1).

$(\text{TAP})\text{Co}-\text{C}(\text{CH}_3)_2\text{CN}$ (**3**) is also observed to form and achieve a steady state concentration from reaction of $(\text{TAP})\text{Co}^{\text{II}*}$ ($5 \times 10^{-3} \text{ M}$), $\text{CH}_2=\text{C}(\text{CH}_3)\text{CN}$, (0.14 M) and azo compounds that produce radicals of the form $\cdot \text{C}(\text{CH}_3)(\text{R})\text{CN}$ where R is a sterically demanding substituent (Figure 1). This reaction is based on our previous studies which have demonstrated that $(\text{TAP})\text{Co}^{\text{II}*}$ and radicals of the general structure $\cdot \text{C}(\text{CH}_3)(\text{R})\text{CN}$ react with alkenes to form (organo) $(\text{TAP})\text{Co}$ complexes at a rate equal to the rate of radical formation.¹³ $(\text{TAP})\text{Co}^{\text{II}*}$ rapidly and efficiently reacts with $\cdot \text{C}(\text{CH}_3)(\text{R})\text{CN}$ to form $(\text{TAP})\text{Co}-\text{H}$ which subsequently rapidly adds with methacrylonitrile to form $(\text{TAP})\text{Co}-\text{C}(\text{CH}_3)_2\text{CN}$, which then achieves equilibrium with

Scheme 3



$(\text{TAP})\text{Co}^{\text{II}*}$ and $\cdot \text{C}(\text{CH}_3)_2\text{CN}$ (Scheme 3; Figure 2). Effectively all of the initially formed radicals are converted to $\cdot \text{C}(\text{CH}_3)_2\text{CN}$ by reactions of $(\text{TAP})\text{Co}$ species. Efficient conversion of the initial radical ($\cdot \text{C}(\text{CH}_3)(\text{R})\text{CN}$) occurs in part because the concentration of $(\text{TAP})\text{Co}^{\text{II}*}$ is at least 10^5 times the radical concentration such that reactions with $(\text{TAP})\text{Co}^{\text{II}*}$ are far more probable than bimolecular coupling and disproportionation reactions that terminate the initial radical. An additional requirement is that the initial radical ($\cdot \text{C}(\text{CH}_3)(\text{R})\text{CN}$) not produce an (organo) $(\text{TAP})\text{Co}$ complex that significantly competes with **3**. Under the conditions of these studies, the radicals from VAZO-52 ($\cdot \text{C}(\text{CH}_3)(\text{CH}_2\text{CH}(\text{CH}_3)_2)\text{CN}$) and V-70 ($\cdot \text{C}(\text{CH}_3)(\text{CH}_2\text{C}(\text{CH}_3)_2\text{OCH}_3)\text{CN}$) fulfill this criterion because the only $(\text{TAP})\text{Co}$ species observed are $(\text{TAP})\text{Co}^{\text{II}*}$ and $(\text{TAP})\text{Co}-\text{C}(\text{CH}_3)_2\text{CN}$. The purpose for using VAZO-52 and V-70 in place of AIBN is that they provide lower temperature sources of radicals which permit extending the equilibrium studies to lower temperature.

Steady state concentrations of **1**–**3** were measured using VAZO-52 and V-70 as initial radical sources in the manner described above for the AIBN reactions and used in deriving equilibrium constants for the homolysis of **3** at 296 and 279 K. Equilibrium constants at 296 K evaluated from use of three different initial radical sources (AIBN, VAZO-52, V-70) are in substantial agreement (Table 1).

Thermodynamic values for the homolytic Co-C bond dissociation for $(\text{TAP})\text{Co}-\text{C}(\text{CH}_3)_2\text{CN}$ ($\Delta H^\circ = 18 \pm 1 \text{ kcal mol}^{-1}$, $\Delta S^\circ = 23 \pm 2 \text{ cal K}^{-1} \text{ mol}^{-1}$) were derived from the temperature dependence of the equilibrium constants (Figure 2; Table 1). A total of 14 K values at three temperatures where the concentration of $\cdot \text{C}(\text{CH}_3)_2\text{CN}$ varies by a factor of 30 were used in deriving the $(\text{TAP})\text{Co}-\text{C}(\text{CH}_3)_2\text{CN}$ bond dissociation enthalpy (Figure 2; Table 1).

Activation Parameters for Co-R Bond Homolysis from NMR Line Broadening. NMR spectra for diamagnetic species ($\text{X}-\text{Y}$) in exchange with paramagnetic homolysis products ($\text{X}\cdot$, $\text{Y}\cdot$) experience exchange broadening for nuclei that are strongly coupled with the unpaired electron in one of the paramagnetic species.¹⁴ The expression that describes this situation is given by $(T_2^{-1}(\text{EX}) = \tau_d^{-1}[(A\tau_p/2)^2][1 + (A\tau_p/2)^2]^{-1})$,¹⁴ which reduces to $T_2^{-1}(\text{EX}) = \tau_d^{-1}$ for nuclei in paramagnetic species where the mean lifetime (τ_p) is long and the electron-nuclear coupling constant (A radians s^{-1}) is large ($(A\tau_p/2)^2 \gg 1$). The apparent mean lifetime for the diamagnetic species (τ_d) that results from the observed $T_2^{-1}(\text{EX})$ yields the rate constant ($\tau_d^{-1} = k_{\text{app}}$) for bond homolysis events that result in paramagnetic species that produce efficient nuclear relaxation ($(A\tau_p/2)^2 \gg 1$).

The ^1H NMR for $(\text{TAP})\text{Co}-\text{C}(\text{CH}_3)_2\text{CN}$ was examined from 253 to 353 K, and significant line broadening was observed to occur above 295 K (Figure 4). The line width for the high-field CH_3 singlet ($\delta = -5.0$) for the $-\text{C}(\text{CH}_3)_2\text{CN}$ group is virtually constant from 253 to 290 K ($\Delta\nu_{1/2} = 2.8 \pm 0.2 \text{ Hz}$) and then increases dramatically as the temperature increases from 300 to 333 K ($\Delta\nu_{1/2}(333 \text{ K}) = 78 \pm 2 \text{ Hz}$) and becomes too broad for

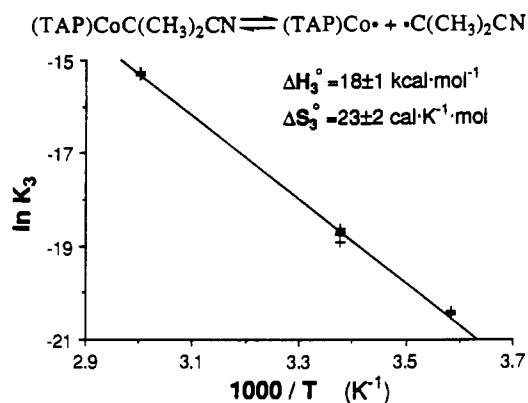
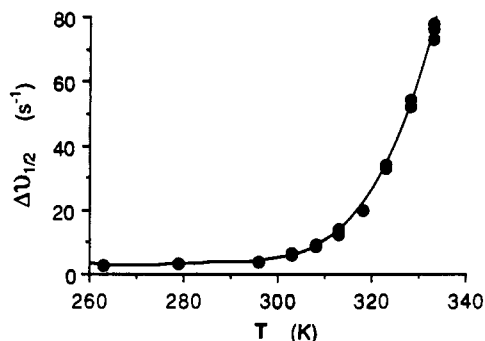
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Table 1. Representative Data for the Determination of the Equilibrium Constants for Homolytic Dissociation of (TAP)Co–C(CH₃)₂CN^a

In	[In] _i (M)	T (K)	[Co ^{II*}]/[CoR]	V ^b (M s ⁻¹)	2k _t ^c (M ⁻¹ s ⁻¹)	[R*] ^d (M)	K ^e
AIBN	0.08	333	11.7	1.1 × 10 ⁻⁶	2.66 × 10 ⁹	2.01 × 10 ⁻⁸	2.4 × 10 ⁻⁷
	0.16		7.7	2.2 × 10 ⁻⁶		2.88 × 10 ⁻⁸	2.2 × 10 ⁻⁷
	0.32		5.68	4.5 × 10 ⁻⁶		4.11 × 10 ⁻⁸	2.3 × 10 ⁻⁷
	0.64		3.85	8.9 × 10 ⁻⁶		5.78 × 10 ⁻⁸	2.2 × 10 ⁻⁷
AIBN	0.08	296	5.56	4.9 × 10 ⁻⁹	2.34 × 10 ⁹	1.45 × 10 ⁻⁹	8.0 × 10 ⁻⁹
	0.16		3.62	1.0 × 10 ⁻⁸		2.07 × 10 ⁻⁹	7.5 × 10 ⁻⁹
	0.32		2.56	1.8 × 10 ⁻⁸		2.77 × 10 ⁻⁹	7.1 × 10 ⁻⁹
	0.64		1.75	4.1 × 10 ⁻⁸		4.19 × 10 ⁻⁹	7.3 × 10 ⁻⁹
VAZO-52	0.76	296	1.11	7.2 × 10 ⁻⁸	2.34 × 10 ⁹	5.56 × 10 ⁻⁹	6.2 × 10 ⁻⁹
	0.64		0.53	2.9 × 10 ⁻⁷		1.19 × 10 ⁻⁸	6.3 × 10 ⁻⁹
V-70	0.0625	296	0.42	6.7 × 10 ⁻⁷	2.34 × 10 ⁹	1.69 × 10 ⁻⁸	7.1 × 10 ⁻⁹
	0.0290		0.61	3.1 × 10 ⁻⁷		1.15 × 10 ⁻⁸	7.0 × 10 ⁻⁹
V-70	0.0625	279	0.31	4.4 × 10 ⁻⁸	2.13 × 10 ⁹	4.57 × 10 ⁻⁹	1.4 × 10 ⁻⁹
	0.115		0.21	8.1 × 10 ⁻⁸		6.17 × 10 ⁻⁹	1.3 × 10 ⁻⁹

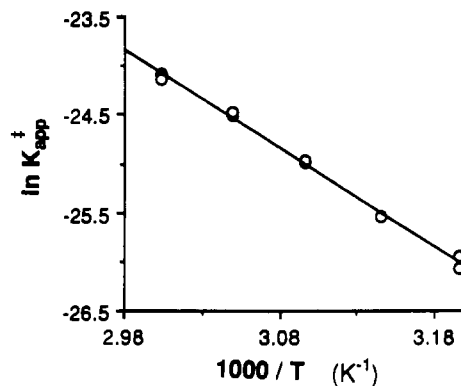
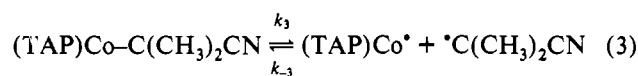
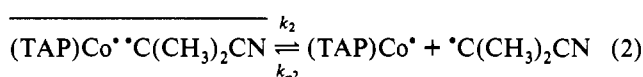
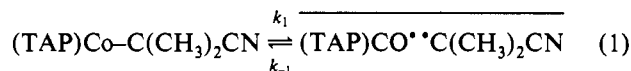
^a In is the radical source. [(TAP)Co^{II*}]_i = 5.0 × 10⁻³ M. [Co^{II*}]/[Co-R] is the ratio of the molar concentration of (TAP)Co^{II*} to that of (TAP)Co–C(CH₃)₂CN in equilibrium with •C(CH₃)₂CN in CHCl₃ obtained by reaction of (TAP)Co^{II*} and CH₂=C(CH₃)₂CN with initiator radicals. ^b V is the rate of radical production (k_i[radical source]). ^c k_t is the rate of self-termination for •C(CH₃)₂CN radicals. ^d Molar concentration of •C(CH₃)₂CN in CHCl₃ at temperature T. ^e Equilibrium constant for dissociation of (TAP)Co–C(CH₃)₂CN into (TAP)Co* and •C(CH₃)₂CN in CHCl₃ at temperature T.

**Figure 2.** Van't Hoff plot for the homolytic dissociation of (TAP)Co–C(CH₃)₂CN in chloroform.**Figure 3.** Temperature dependence of the observed line width at half-height (Δν_{1/2}, s⁻¹) for the cyanoisopropyl methyl resonance (δ = -5.0 ppm) of (TAP)Co–C(CH₃)₂CN in chloroform.

accurate determination at higher temperatures (Figure 3). The line broadening is ascribed to exchange of (TAP)Co–C(CH₃)₂CN with its paramagnetic homolysis products, (TAP)Co^{II*} and •C(CH₃)₂CN. Figure 4 illustrates the use of T₂⁻¹(EX) measurements in conjunction with transition state theory to provide activation parameters for the process that involves the homolytic dissociation of (TAP)Co–C(CH₃)₂CN (ΔH^{*}_{app} = 20 ± 1 kcal mol⁻¹, ΔS^{*}_{app} = 13 ± 2 cal K⁻¹ mol⁻¹).

Discussion

Homolytic bond dissociation for (TAP)Co–C(CH₃)₂CN in solution proceeds through solvent-caged radical pairs (eqs 1 and 2; Figure 5). The overall homolytic dissociation of (TAP)Co–C(CH₃)₂CN is depicted by eq 3. Equilibrium measurements in this article directly correspond to the evaluation of K₃ (eq 3), which

**Figure 4.** Determination of activation parameters for homolytic dissociation of (TAP)Co–C(CH₃)₂CN in chloroform by NMR T₂⁻¹(EX) measurements and transition state theory (K^{*}_{app}(h/kT); k_{app} = 1/τ_d).

provides thermodynamic values for the homolytic (Co–C) bond dissociation process (ΔH^o₃ = 18 ± 1 kcal mol⁻¹, ΔS^o₃ = 23 ± 2 cal K⁻¹ mol⁻¹) (eq 3). The (TAP)Co–C(CH₃)₂CN bond dissociation enthalpy of 18 kcal is in the lower range of Co–C values,^{5,9} which is compatible with the relatively large steric demands and stability of the •C(CH₃)₂CN radical.

Interpretation of the thermodynamic parameters is unequivocal, but occurrence of an intermediate radical pair (TAP)Co*•C(CH₃)₂CN complicates interpretation of the apparent rate and activation parameters for bond homolysis (k_{app}, ΔH^{*}_{app}, ΔS^{*}_{app}) obtained from ¹H NMR line broadening for (TAP)Co–C(CH₃)₂CN (Figure 4). Line broadening for the methyl resonance of the –C(CH₃)₂CN fragment in **2** could be produced by homolysis of **2** to form paramagnetic species either in the radical pair (Co*•R) or in the bulk solution (Co* + R*) or both. The contribution to T₂ is dependent on the coupling constant for the nucleus observed (A_H) and the lifetime of the paramagnetic species (τ_p) (T₂⁻¹(EX) = τ_d⁻¹[Aτ_{p/2}]²[1 + (Aτ_{p/2})²]⁻¹). The •C(CH₃)₂CN radical has a large methyl hydrogen coupling constant (A_H = 59 MHz = 370 × 10⁶ radians

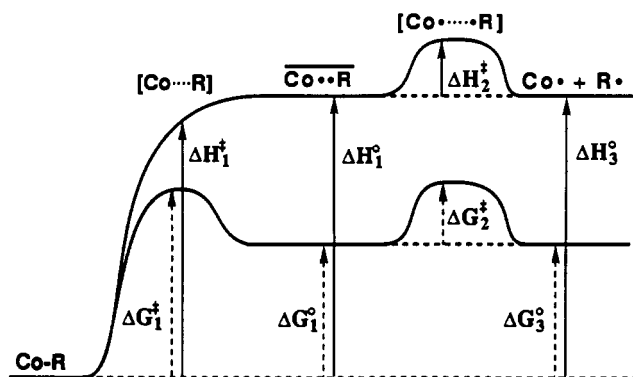


Figure 5. Free energy and enthalpy reaction coordinate diagrams for Co-R bond homolysis illustrating the transition states for bond homolysis to enter a caged radical pair and separation of the caged pair into freely diffusing radicals.

s^{-1}),¹⁵ which gives $(A_H\tau_p/2)^2 \gg 1$ for the freely diffusing radical ($\tau_p > 10^{-7}$ s) but $(A_H\tau_p/2)^2 < 1$ for the short-lived radical pair ($\tau_p < 10^{-9}$ s). This indicates that only the fraction of homolysis events that result in freely diffusing $\cdot C(CH_3)_2CN$ should contribute to reducing the apparent mean lifetime (τ_d) observed for the metal hydrogen nuclei in (TAP)Co-C(CH₃)₂CN. The meaning of k_{app} from NMR line broadening is thus probably the same as that for kinetic methods that are based on trapping of radicals that enter the bulk solution where k_{app} is given by the product of the rate constant for radical pair formation (k_1) and the fraction of radical pairs that separate into radicals in solution ($k_{app} = k_1 k_2 / (k_{-1} + k_2) = k_3$). An estimate for k_{-3} can be obtained by combining the value for k_3 from NMR line broadening with K_3 from direct equilibrium measurements ($k_{-3} = k_3 / K_3 = k_{-1} k_2 / (k_{-1} + k_2)$). The value of 1.0×10^9 for k_{-3} (333 K) (k_3 (333 K) = $236 s^{-1}$; K_3 (333 K) = 2.3×10^{-7}) is compatible with values obtained for reactions of Co^{II} and R[•] species using time-resolved spectroscopic methods.^{9,16} The activation parameters (ΔH^*_{app} , ΔS^*_{app}) are a composite of the values for the fundamental processes (eqs 1 and 2), and the detailed interpretation requires knowledge of the rate constants for radical pair separation (k_2) and recombination (k_{-1}).^{10,11} The apparent activation entropy ($\Delta S^*_{app} = 13 \pm 2 \text{ cal K}^{-1} \text{ mol}^{-1}$) is in the range expected for a dissociative process ($\Delta S^*_3 = 23 \pm 2 \text{ cal K}^{-1} \text{ mol}^{-1}$), where ΔS^*_1 makes the predominant contribution. The apparent activation enthalpy ($\Delta H^*_{app} = 20 \pm 1 \text{ kcal mol}^{-1}$) is dominated by the bond homolysis activation enthalpy (ΔH^*_1) and is $\sim 2 \text{ kcal mol}^{-1}$ larger than the solution bond homolysis enthalpy ($\Delta H^*_3 = 18 \pm 1 \text{ kcal mol}^{-1}$). A difference of $\sim 2 \text{ kcal mol}^{-1}$ between ΔH^*_{app} and the solution bond dissociation enthalpy is a recurring theme for Co-R bond homolysis reactions in low viscosity solvents⁸ and primarily results from a contribution to ΔH^*_{app} from the activation enthalpy for caged radical pair separation ($k_{-1}(k_2 + k_{-1})^{-1}\Delta H^*_2$).^{10,11} assuming that differential solvation enthalpies are negligible.

Continuing studies in this area are focused on exploring solvent effects and the scope of application for both the equilibrium and NMR exchange broadening methods in organo-metal homolysis processes.

Experimental Section

Materials. (TAP)Co (Aldrich) was recrystallized from chloroform-heptane. Methacrylonitrile (MAN) of 99% purity (Aldrich) was purified by multiple vacuum distillations to remove the stabilizer immediately before use. AIBN (2,2'-azobis(isobutyronitrile)) (Kodak), VAZO-52 (2,2'-azobis(2,4-dimethylpentanenitrile)) (DuPont), V-70 (2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile)) (Wako Chemicals), and CDCl₃ (Aldrich) were used as received.

General Procedures. In a typical reaction procedure, 3.75 mg of (TAP)-Co, methacrylonitrile, and initiator were added to 1 mL of CDCl₃ in

air, and the resulting mixture was divided into two equal portions. One sample was transferred to a vacuum-adapted NMR tube. After three freeze-pump-thaw cycles, the tube was sealed and immersed in a constant-temperature bath (± 0.1 °C) for kinetic and thermodynamic studies. 1-Hexyne or 5-hexynenitrile (0.02 mL) was added to the second sample of the reaction mixture, and the resulting sample was transferred to an NMR tube, which was sealed in the same manner as the first-sample tube. The purpose of preparing the second sample was to measure the rate of free radical production under the conditions of the kinetic and thermodynamic studies.

As reported in an earlier paper,¹³ 1-hexyne and 5-hexynenitrile are effective (por)Co-H scavengers that form very stable vinylcobalt porphyrin complexes so that the rate of (por)Co-R formation equals the rate of free radical production measured with the stable radical 2,2',6,6'-tetramethylpiperidine-1-oxyl (TEMPO).¹⁷

Conversion of (TAP)Co^{II} to organocobalt porphyrin derivatives was monitored by comparison of the phenyl meta proton signal of (TAP)Co^{II} at 9.4 ppm with the phenyl ortho proton signals of (TAP)Co-C(CH₃)₂CN at 8.0 ppm using a 200-MHz NMR spectrometer. The rate of free radical production, V , was used in determining the concentration of free radicals at steady state by the relationship $[R^*] = (V/2k_t)^{1/2}$, where k_t is the rate constant for cyanoisopropyl radical termination. Self-termination constants (k_t) for $\cdot C(CH_3)_2CN$ at a series of temperatures were obtained from literature results^{12a} demonstrating that k_t is diffusion controlled and adapted for the viscosity of chloroform.

Using published data for the dependence of k_t on viscosity^{12a} and the temperature dependence of chloroform viscosity,¹⁸ values of k_t for chloroform solutions were obtained (Table 1). The concentrations of (TAP)Co^{II} and (TAP)Co-C(CH₃)₂CN at 278 and 296 K were determined at equilibrium in the NMR spectrometer. Severe line broadening at 333 K introduces large errors in the concentration measurements and requires locking-in the equilibrium concentrations of 1 and 3 by rapidly quenching to lower temperatures (279–295 K) where the ¹H NMR could be recorded without serious line broadening. By observation of the slow reestablishment of equilibrium over a period of hours to days at the lower temperatures, it was shown that this procedure was appropriate for obtaining the equilibrium concentrations of 1 and 3 at 333 K, provided that the NMR scanning time was less than ~ 20 min at 296 K and 1 h at 279 K. This procedure provides an adequate description of the equilibrium concentrations of 1 and 3 at the higher temperature (333 K) because the radical 2 is the limiting reagent and there are insufficient radicals produced during the cooling and observation of the NMR to significantly change the concentrations of 1 and 3, which are $\sim 3 \times 10^{-3}$ M. As the temperature is lowered, the equilibrium constant to form the organometallic 3 increases and the rate of radical production from AIBN decreases (Table 1). Most of the radicals formed from AIBN during the time for cooling and recording of the NMR spectrum react with (TAP)Co^{II} to form (TAP)Co-C(CH₃)₂CN in an effort to reestablish equilibrium at the lower temperature. The rate of formation of the radical 2 at 296 K (5×10^{-9} – $4 \times 10^{-8} \text{ M s}^{-1}$) is sufficiently small that a relatively long time period ($\sim 10^4$ s) is required to result in a significant change in the relatively large concentration of (TAP)Co^{II} present at 333 K ($(3\text{--}5) \times 10^{-3}$ M). Experiments using the highest concentrations of AIBN were performed at 296 and 279 K and found to agree within the experimental error ($\pm 5\%$). At 279 K a period of several hours is needed to produce $10^{-4} \text{ mol L}^{-1}$ of radicals.

Line broadening was measured for the methyl proton signal of the organic substituent of (TAP)Co-C(CH₃)₂CN at -5.0 ppm. ¹H NMR studies in CDCl₃ at elevated temperatures were carried out in medium-walled NMR tubes (Wilmad) sealed below the spinner such that the entire solution was thermostated. Sealing the sample tubes was accomplished by first fixing the top and bottom of the tube such that they remained concentric and then collapsing the walls of the tube containing the frozen sample solution. The tube was sealed at a position where the sample was confined below the spinner which minimizes thermal gradients in the sample.

Acknowledgment. This work was supported by the National Science Foundation and a DuPont Senior Research Fellowship for A.A.G. The gift of V-70 from Wako Chemicals is gratefully acknowledged.

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