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Kinetic Model for the Reaction of Cobalt Porphyrins with Olefins under Free Radical Conditions[1]

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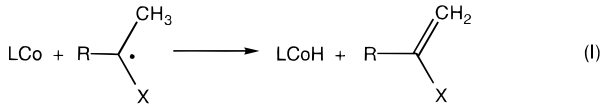
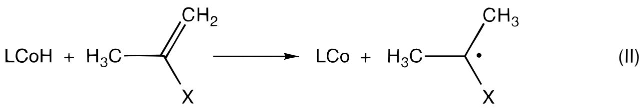
A general kinetic model to describe the interaction of two dissimilar olefins with cobalt(II) tetrakis(anisyl)porphyrin complexes in the presence of organic radicals has been developed. The kinetic scheme presumes the formation of organometallic products both by radical addition to Co(II) and by reaction of hydridocobalt(III) complexes with the corresponding olefins. The proposed general mechanism also presumes that cobalt hydride is formed by two pathways—either by bimolecular reaction of the Co(II) porphyrin complex with the radical or by unimolecular β-hydrogen atom elimination from the organocobalt(III) species. The general model is then modified to the specific case of competition between methacrylonitrile and aliphatic olefins. On application of the simplifying assumption that most of the hydride forms through the bimolecular reaction and that both olefins follow the same predominant reaction pathways, a model describing the concentration of organometallic species derived from both olefins is developed. This dependence allows the evaluation of some elementary relative reaction rate constants for organometallic dissociation and reactions of the olefins with the hydridocobalt complex. It is shown that, despite the observation that the products derived from simple olefins such as cyclopentene are formed at much higher steady-state concentrations, methacrylonitrile reacts with hydridocobalt(III) at more than 25 times the rate of those simple olefins. Limitations on applying the developed methods of rate constant measurements have also been considered.

Introduction

Chain transfer catalysis is a method for controlling molecular weight in free radical polymerization of certain monomers, primarily methacrylates.[2] It can be described as the combination of reactions I and II, where





LCo is a cobalt(II) chelate, (R)(CH_3)(X)$C^{\bullet}$ is a propagating radical, and X is CN, Ph, or CO_2CH_3. Radicals formed during the free radical polymerization process propagate by addition of monomer, forming longer chain radicals until they react with a cobalt chelate molecule. The net effect of the reaction is to abstract a hydrogen atom from a growing polymer radical and transfer it to a new monomer, which then initiates a new propagating polymer chain. These reactions provide a catalytic method of reducing the molecular weight in free radical polymerization of methacrylates and related monomers without the use of stoichiometric chain transfer reagents and high levels of initiators.[3] The hydridocobalt chelate (LCoH) is an assumed but unobserved intermediate species.[4] In efficient reactions, the catalyst can achieve tens of thousands of turnovers[5] with no visible degradation of the catalyst, indicating the general absence of side reactions involving cobalt.

The result of the catalysis is a mixture of oligomer or polymer molecules, each with a terminal double bond. These species can be utilized as macromonomers for copolymerization with other monomers.[6] The rate

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(1) Contribution No. 7039 from DuPont Central Research. Work originated by A.A.G. at the University of Pennsylvania and completed at DuPont CR&D.

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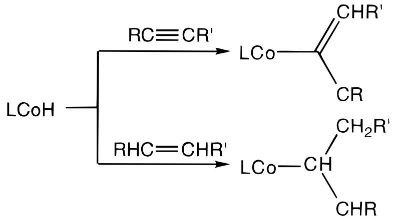
constant of reaction I in the case of methyl methacrylate has been determined to be on the order of 10^6-10^8 M^{-1} s^{-1}.[7] Thus, it is possible to prepare oligomers with very low concentrations of initiator and without sulfur or related transfer agents which can impart undesirable properties to the finished products. In addition to its commercial importance, catalysis of chain transfer is an area of interesting research because it presents a unique opportunity to simultaneously obtain fundamental information on elementary reactions of both organometallic and free radical species. When two or more olefins are employed in the free radical polymerizations under chain transfer catalysis, the distribution of products is controlled by the kinetic competitions set up in the system. Thus, it is essential to understand the kinetics not only of chain transfer with individual monomers but also with the mixed monomers.

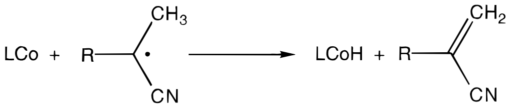
Initial investigations of chain transfer catalysis (CTC) were based primarily upon product analysis.[5a,6b,8] The concentrations of presumed intermediate organometallic species were well below the limits of instrumental sensitivity. In a previous paper,[9] we described a synthetic application of conditions like those of CTC. It makes available a variety of organocobalt porphyrin and phthalocyanin complexes by means of reaction III or IV,



(III)

$$\mathrm{LCoH + RHal + B \longrightarrow LCoR + B\text{-}H^{+} + Hal^{-}} \qquad \text{(IV)}$$

where X is halide and B is a donor molecule such as DMF. The hydridocobalt chelate required for the syntheses in (III) and (IV) is obtained *in situ* by reaction of the corresponding Co(II) chelate with tertiary radicals having methyl hydrogen atoms available (reaction V).



(V)

Tertiary radicals for reactions III−V are conveniently generated by thermal decomposition of commercially available azo initiators commonly used in free radical polymerizations. The tertiary radical mediated synthesis of organocobalt chelates not only provides a one-pot method for preparation of a variety of organocobalt chelates but also affords valuable information on the mechanisms and behavior of cobalt-catalyzed reactions under CTC conditions.

An important feature of chain transfer catalysis is that, in the presence of an olefin, acetylene, or alkyl halides, the cobalt hydride converts exclusively into LCoR species. Side reactions such as (VI)−(VIII) are

$$\mathrm{2LCoH \rightarrow 2LCo + H_2} \qquad \text{(VI)}$$

$$\mathrm{LCoH + R \rightarrow LCo + R{-}H} \qquad \text{(VII)}$$

$$\mathrm{LCoR + R^{*} \rightarrow LCo} + \text{non-radical product} \qquad \text{(VIII)}$$

not detected, despite the fact that they are known under some conditions.[10] The relative unimportance of these reactions was indicated by the fact that the rates of reactions III and IV for certain olefins and most acetylenes were identical with the rate of free radical production. Side reactions (VI)−(VIII) would consume radicals without production of organocobalt(III) porphyrin species, thus causing the rate of reactions III and IV to be less than the rate of free radical generation. The fact that these side reactions can be negligible under the conditions employed significantly simplifies the potential reaction scheme for the interaction of free radicals with cobalt porphyrins and olefins.

The use of tertiary radicals in organometallic synthesis can serve as a good model for CTC, provided that

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the organocobalt chelate formed is observable but relatively unstable. It should be more stable than, for example, LCo−C(CH_3)$_2$($COOCH_3$), which is presumably formed during CTC in methyl methacrylate polymerizations but is unobserved spectroscopically. On the other hand, experimental conditions should be chosen in a way as to prevent the transformation of all of the Co(II) species into organometallic Co(III) species. For instance, reactions with methyl acrylate form stable LCo−CH(CH_3)($COOCH_3$), converting essentially all of the Co(II) to Co(III) and terminating the catalytic reaction. An excess of Co(II) chelate is necessary to keep a model reaction system close to the polymeric prototype, but more importantly, the stability of the Co−C bond should be only slightly greater than that of LCo−C(CH_3)$_2$($COOCH_3$). Simple alkenes meet both of these requirements. It is noteworthy that they do not polymerize during radical syntheses, thereby avoiding complications arising from the variations in the molecular size (and therefore molecular diffusivity) of substituents adjacent to the double bond. The influence of steric hindrance in the olefinic component as well as molecular weight and diffusion on the rate constants of CTC will be the subject of a separate study.

The kinetic scheme proposed below is designed to describe the reaction system involving olefins and radicals of different reactivities to define the limits of the system. Methacrylonitrile is an olefin polymerizable by free radical techniques, and its radical is relatively stable. Aliphatic olefins are not readily polymerized by free radical techniques because their radicals are far more energetic and reactive. During CTC there are almost always two or more olefins present in the reaction mixture at any moment of reaction—for instance, the monomer and its oligomers or the olefin derived through reaction V from the initiating radical if it is different from the olefin being studied. If CTC is conducted under conditions of copolymerization, the number of olefins of differing reactivity increases dramatically. Previous kinetic schemes for CTC[2a−c,11] considered only the single-olefin case; thus, the present kinetic scheme is a step toward development of a more general mechanism.

Experimental Section

Materials. Olefins (Aldrich) were purified by multiple vacuum distillation immediately prior to use. Deuteriochloroform (Aldrich) was used as a solvent without additional purification. [Tetrakis(*p*-methoxyphenyl)porphyrinato]cobalt(II) ((tetraanisylporphyrinato)Co(II) or (TAP)Co (Aldrich)) was recrystallized twice from chloroform−heptane.

AIBN (2,2′-azobis(isobutyronitrile)) (Eastman Kodak), VAZO-52 (2,2′-azobis(2,4-dimethylpentanenitrile)) (Du Pont), 1,1′-azobis(cyclohexanecarbonitrile) (Aldrich), and V-70 (2,2′-azobis(4-methoxy-2,4-dimethylpentanenitrile)) and V-601 (2,2′-azobis(2-methyl propionate)) (both Wako Chemicals) were used as received and were stored at −10 °C.

Kinetic Measurements. All reagents were mixed in air and transferred into an NMR tube adapted for vacuum. After three freeze−pump−thaw cycles to 10^{-3} Torr vacuum, the tubes were sealed and immersed into a constant-temperature bath (controlled to ±0.1 °C at whatever temperature is indicated in the text). To measure the rate of free radical production under the conditions of the kinetic studies, a CoH trapping technique was applied. A sample of 1-hexyne was added to the reaction mixture. As reported in an earlier paper,[9] 1-hexyne is effective as a scavenger for LCo−H by formation of very stable vinylcobalt porphyrin complexes. The rate of LCo−R formation equals the rate of free-radical production, as measured with the stable radical 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO), but is more applicable to the conditions of this study.[9]

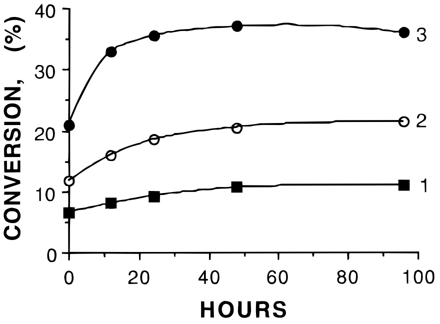

Figure 1. Conversion of (TAP)Co to (TAP)Co−C(CH_3)$_2$-CN as a function of time at 23 °C after the temperature was held at 60 °C for 30−60 min. (The initial points reflect the steady-state concentrations of **1** at 60 °C. See Experimental Section.) Conditions: initial concentration of (TAP)-Co 4.7 × 10^{-3} M, $CDCl_3$ solvent, [AIBN] = 0.04 M (1), 0.16 M (2), 0.64 M (3).

The rate of free-radical production, *V*, was used to determine the equilibrium constant of organocobalt porphyrin formation from cobalt porphyrin and free radicals. Under the steady-state conditions employed, the relationship is $K_1 = \{[CoR_1](2k_{T1})^{1/2}\}/\{[Co]V^{1/2}\}$, where k_{T1} is the rate constant for cyanoisopropyl radical termination. Self-termination constants (k_{T1}) for $^{\bullet}C(CH_3)_2CN$ at a series of temperatures were obtained from literature results;[12] k_{T1} is diffusion-controlled and has been modified for the viscosity of chloroform at the temperatures used in this study.

Conversion of $[(TAP)Co^{II}]^{\bullet}$ to organocobalt porphyrin derivatives was monitored using a 200 MHz NMR spectrometer by comparison of its meta phenyl proton signal at ~9.4 ppm with that of pyrrolic protons of the Co(III) compounds, 9.0 ppm for (TAP)CoC(CH_3)$_2$CN (**1**) and at 8.86 ppm for (TAP)CoR (**2** for the general case, **2-Hex** for hexyl, **2-CyH** for cyclohexyl, etc.). For systems where all species remain soluble, this method of quantification provides relative concentrations of $[(TAP)Co^{II}]^{\bullet}$ and organo-Co(III) species.

Severe line broadening of the proton resonance of **1** at temperatures of 60 °C and above introduces substantial uncertainty into the concentration measurements. This uncertainty can be overcome by quenching the equilibrium concentrations of the organometallics by rapidly cooling to room temperature or below, where the ^{1}H NMR could be recorded without serious line broadening. By observation of the slow reestablishment of equilibrium at the lower temperatures (Figure 1), it was shown that this procedure was appropriate for obtaining the concentrations of cobalt porphyrins at 40 and 60 °C, provided that the NMR scanning time at 23 °C was less than 10 min.

Results

The complex (TAP)CoC(CH_3)$_2$CN (**1**) and the related alkylcobalt(III) species (TAP)CoR (**2**) are generated by the reaction of the cobalt(II) complex (TAP)Co^{II} (**3**) with

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Table 1. Representative Data for the Determination of the Equilibrium Constants (K_1) for (TAP)Co−C(CH$_3$)$_2$CN Formation

azo initiator	temp (°C)	[CoR]/[Co]$V^{1/2\ a,b}$	$2k_{T1}{}^{c}$ ($M^{-1}\ s^{-1}$)	$K_1{}^{d}$
AIBN	60	84	2.66×10^9	4.33×10^6
AIBN	23	2830	2.34×10^9	1.37×10^8
VAZO-52	23	3420	2.34×10^9	1.66×10^8
V-70	23	2930	2.34×10^9	1.42×10^8
V-70	6	15300	2.13×10^9	7.08×10^8

[a] [CoR]/[Co] is the ratio of the molar concentration of (TAP)Co−C(CH$_3$)$_2$CN to (TAP)Co in equilibrium with •C(CH$_3$)$_2$CN in CDCl$_3$ obtained from Figure 2. [b] V is the rate of radical production measured by trapping with 1-hexyne as described in refs 9b and 11c. [c] k_{T1} is the rate of self-termination for •C(CH$_3$)$_2$CN radicals. Data from ref 12a are adapted for the viscosity of chloroform. [d] Equilibrium constant for formation of (TAP)Co−C(CH$_3$)$_2$CN from (TAP)Co and •C(CH$_3$)$_2$CN in chloroform.

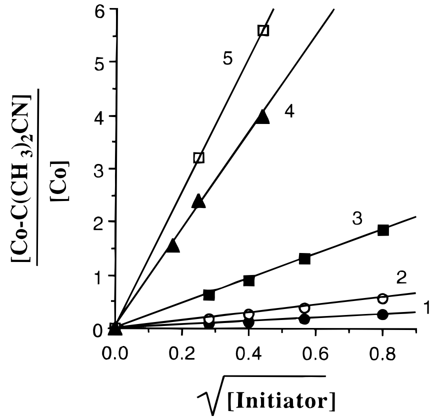
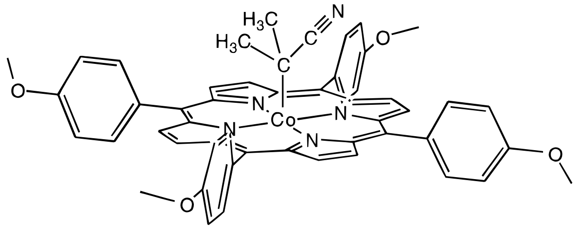


Figure 2. Concentration of (TAP)Co−C(CH$_3$)$_2$CN at steady state as a function of the square root of the concentration of the azo initiator (CDCl$_3$, initial concentration of (TAP)Co 4.7×10^{-3} M; [MAN] = 0.14 M): (1) AIBN, 60 °C; (2) AIBN, 23 °C; (3) VAZO-52, 23 °C; (4) V-70, 23 °C; (5) V-70, 6 °C.

olefins in the presence of the cyanoisopropyl radical, (CH$_3$)$_2$(CN)C• (**4**), generated from AIBN. It is presumed that this reaction takes place through the intermediacy of the hydridocobalt(III) complex (TAP)CoH (**5**). Radical **4** was used throughout this study unless otherwise noted in the text, because it results in the formation of detectable amounts of **1** at ambient temperatures. When **4** reacts with cobalt porphyrin **3** by pathway I, it yields methacrylonitrile (MAN). For this reason, MAN was the olefin chosen for initial investigation so that there would be only one olefin and one organocobalt(III) complex to follow.



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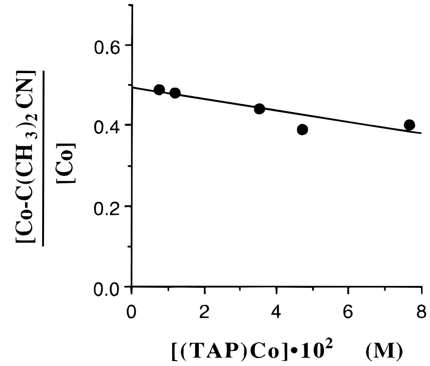


Figure 3. Dependence of the steady-state concentration of (TAP)Co−C(CH$_3$)$_2$CN on the initial concentration of cobalt porphyrin (CDCl$_3$, 23 °C, [AIBN] = 0.32 M).

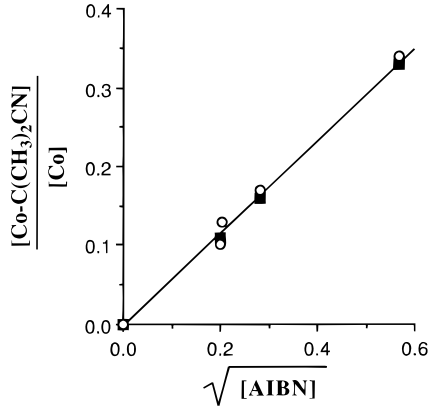


Figure 4. Dependence of the relative concentrations of (TAP)Co−C(CH$_3$)$_2$CN and (TAP)Co at steady state on the square root of the concentration of AIBN without (■) and with (○) addition of MAN (0.14 M) at 23 °C.

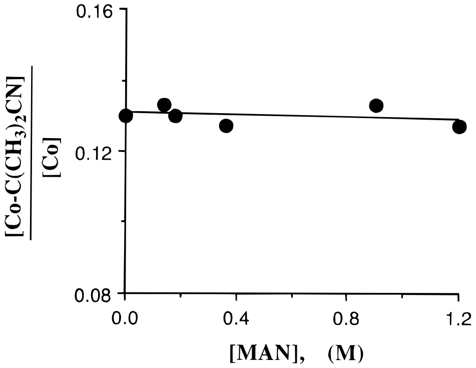
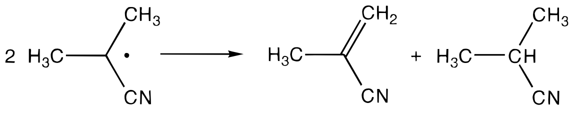


Figure 5. Dependence of the concentration of (TAP)Co−C(CH$_3$)$_2$CN at steady state on the concentration of added MAN (CDCl$_3$, 60 °C, 50 min, [AIBN] = 0.16 M, initial [(TAP)Co] 0.94×10^{-2} M).

When MAN was the only olefin added to a mixture of initiator and Co(II) porphyrin, the relative steady-state concentration of **1** was found to be linearly dependent on the square root of the azo-initiator concentration. This relationship held true regardless of the type of initiator and the temperature of the reaction (Table 1 and Figure 2, the rate of generation of radicals is dependent upon the nature of the initiator and the temperature of the reaction). It was also only slightly dependent on the concentration of the porphyrin in the solution (Figure 3). It is noteworthy that when the initiator was AIBN, the steady-state concentration of **1** was independent of the concentration of MAN, even at concentrations of “zero” (Figures 4 and 5). This “zero” concentration behavior reflects the fact that though no MAN was added to the reaction mixture, the product from addition of the radical to Co(II) is indistinguishable from the product of MAN addition to Co^{III}−H. Additionally, a trace concentration of MAN is rapidly established in the system through the disproportionation of radical **4** with another radical **4** in the radical



(IX)

4 **MAN**

cage immediately upon formation by decomposition of the azo-initiator molecule. Between 10% and 20% of all AIBN-generated radicals are estimated to collapse before leaving the radical cage, but in solution, coupling to the radical dimer is a far more important reaction, accounting for at least 90% of the termination reactions. Reaction IX is relatively unimportant to the termination of radical **4**, accounting for less than 10% of the termination events.[12] The final concentration of MAN obtained by reaction IX is less than or equal to the concentration of (TAP)Co employed in the experiments but is several orders of magnitude less than the concentrations of olefins purposely added. Hence, all measurements, even those with “zero” concentration of MAN obtained during the first few minutes of reaction after attainment of steady state, are accurate.

We have demonstrated elsewhere[9a] that radicals bulkier than the cyanoisopropyl radical from AIBN do not form observable concentrations of Co(III) organometallic species. Table 1 displays very similar equilibrium constants (see below) for (TAP)CoC$(CH_3)_2$CN (**1**) generated in the presence of three different azo initiators at 23 °C. No additional products are observed in the reaction, despite the fact that the initial radicals being generated in each case are different. The rates of generation of radicals for these initiators vary by more than 1 order of magnitude at 23 °C, yet the measured equilibrium constant, K_1, for **1** is essentially the same for all three initiators employed. On the other hand, changing the temperature of the reaction has a profound effect on the steady-state concentrations of **1** and K_1, even though the rates of generation of radicals are now more similar or in some cases equivalent. It is clear that the nature of the tertiary radicals being generated has little effect on the outcome of the reaction, even if they do not form stable organometallic species; they are equally effective as a source of CoH in the system.

In contrast to the behavior of the methacrylonitrile system, the relative concentration of Co(III) alkyls generated from simple, unfunctionalized olefins are linearly dependent on the concentration of the corresponding olefin. For illustration, the ratio of the steady-state concentration of (TAP)Co-2-hexyl (**2-Hx**) relative to **3** increases linearly with increasing concentration of 1-hexene (Figure 6). Unfortunately, this reaction is complicated by the observed presence of the 1-isomer, whose concentration relative to the 2-isomer varies with time.[9] To eliminate the complication of two isomers, cycloolefins were chosen for further study. It should be emphasized that all simple alkenes give qualitatively similar dependencies but that branching or other steric congestion can quickly decrease the stability of the alkyl adducts.

Under steady-state conditions, the [CoR]/[Co] ratio increases linearly with the concentration of radicals for both the cyclohexyl adduct (**2-CyH**) and **1** (Figure 7). The concentration of (TAP)CoC$(CH_3)_2$CN is independent of the concentration of cyclohexene. The data in Figure 8 includes the value of K_1 for complex **1** calculated from the data in Figure 7 in addition to data from systems containing only methacrylonitrile (Table 1); the values obtained in the presence and absence of added cyclohexene are obviously consistent.

Additional information is obtained by varying the relative concentrations of the two olefins (Figure 9). Variation of the ratio of cyclopentene to methacrylonitrile concentration from 0 to 380 shows that the ratio

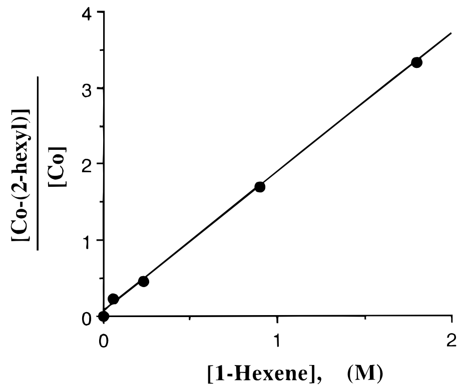


Figure 6. Steady-state concentration of (TAP)Co−(2-hexyl) as a function of the concentration of 1-hexene ($CDCl_3$, 60 °C, initial [(TAP)Co] 0.94 × 10^{-2} M, [AIBN] 0.08 M).

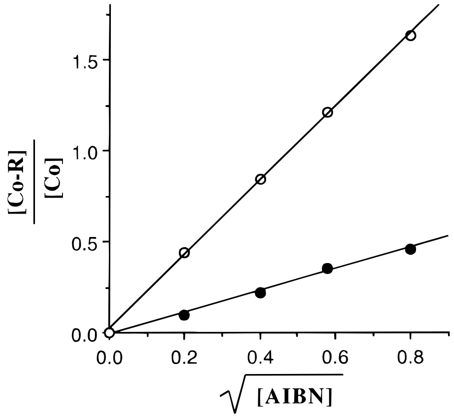


Figure 7. Dependence of the steady-state concentration of (TAP)Co−C$(CH_3)_2$CN (●) and (TAP)Co−cyclohexyl (○) on the square root of the concentration of AIBN ($CDCl_3$, initial [(TAP)Co] 0.94 × 10^{-2} M, [cyclohexene] = 0.4 M, 25 °C, 65 h).

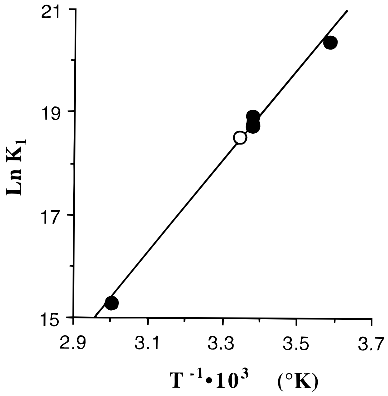


Figure 8. van't Hoff plot for the formation of (TAP)Co−C$(CH_3)_2$CN in chloroform applying the data from Table 1 (●) and Figure 7 (○).

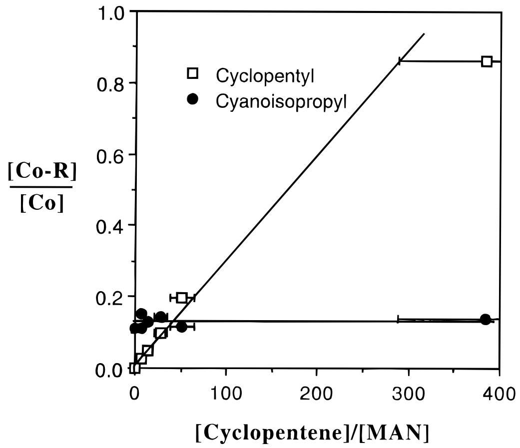
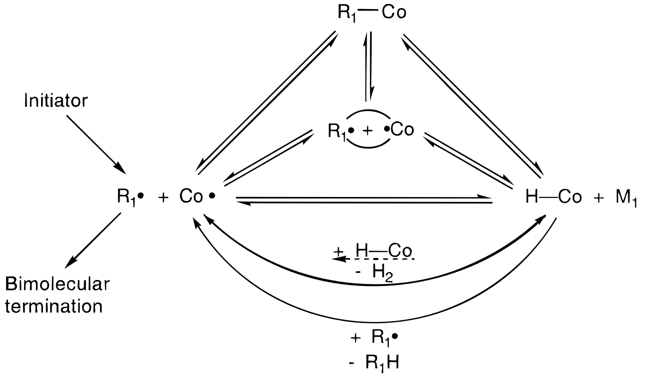


Figure 9. Dependence of the steady-state concentrations of (TAP)Co$-$C$(CH_3)_2$CN (●) and (TAP)Co$-$cyclopentyl (□) on the ratio of molar concentrations of cyclopentene and MAN ($CDCl_3$, 60 °C, initial [(TAP)Co] 0.94×10^{-2} M, [AIBN] = 0.08 M).

Scheme 1



of steady-state concentrations of Co$-$R to **3** is independent of the ratio for **1** but that the concentration of the cyclopentyl adduct **2-CyP** varies linearly with the ratio.

From the experimental observations above, it is clear that there are profound differences in the patterns of reactivity for methacrylonitrile and simple olefins. There is no indication, however, that they undergo fundamentally different reactions. The difference seems to be only in the relative rates of reaction. The development of a model which would explain these results would contribute significantly to the understanding of the processes involved in this system and by extension, to catalytic chain transfer.

Discussion

A comprehensive reaction scheme for the reaction of Co(II) with free radicals in the presence of the respective monomer derived from that radical is shown in Scheme 1. Radicals are generated from the initiator at a rate dependent only upon the stability of the particular initiator employed. Radicals leave the reaction through the normal bimolecular radical reactions of combination to dimer or disproportionation (hydrogen atom transfer) to equal portions of saturated and unsaturated species.[13] These reactions go on in the presence or absence of the metal complex; the cobalt influences the rates only through its effect on the concentrations of available radicals.

In the presence of a Co(II) macrocycle complex such as a cobalt porphyrin or cobalamin, another series of reactions can take place. The radical is very likely to react with Co(II) because the activation energy is low, because Co(II) is essentially a radical species and the Co(II) is present in much larger concentrations than other radical species. The reaction can be considered to be a normal radical$-$radical reaction which can follow either of the two pathways mentioned for the initiator-derived radicals. The observed organometallic product of the reaction, an alkylcobalt(III) species shown at the top of Scheme 1, is the product of combination. In addition, we have developed very strong evidence that the radical generates a reactive but unobserved concentration of hydridocobalt(III). This reaction is the analog of disproportionation, with the other product being the monomer derived from hydrogen atom abstraction. Finally, reaction of the hydridocobalt(III) species with monomer can yield the alkylcobalt(III) compound. It is this set of reactions which we will describe in greater detail in this paper.

In addition to the reactions we describe here, the two reactions illustrated with curved arrows at the bottom of Scheme 1 can become important under some conditions. The upper is the bimolecular reaction of two hydridocobalt complexes to yield dihydrogen and two Co(II). The lower is the bimolecular reaction of a hydridocobalt complex with a radical to yield a saturated organic product and Co(II). We observe neither of these reactions under the conditions employed in this paper, presumably because the concentration of hydridocobalt(III) never reaches the required concentrations for these reactions to become competitive. They will not be discussed further in this paper, but aspects of this chemistry will be described in a subsequent publication.[14]

It is well-established that radical$-$radical chemistry usually goes through a caged radical pair and in some cases this caged pair can influence the outcome of the reaction. Addition of monomer to the hydridocobalt complex in some cases may be concerted and in other cases may entail the intermediacy of radical products. In papers describing isotopic labeling studies,[15] stereospecific additions indicate that if radical intermediates are important, the lifetime of the caged radical pair must be shorter than or comparable to the time required for one molecular rotation. The work described in this paper has purposely been limited to low-viscosity solvents and to small molecules, all of approximately the same dimensions, thereby minimizing the influence of caged radical pairs. In addition, all of the results are steady-state measurements and there is no observation of any component associated with the radical pair. Generally, the concentrations of caged and freely diffusing radicals are linearly dependent, regardless of subsequent chemistry and especially in low-viscosity media. As a result, inclusion of the distinction of solvent-caged and free radicals in further derivations in this paper would simply add constant terms to all of

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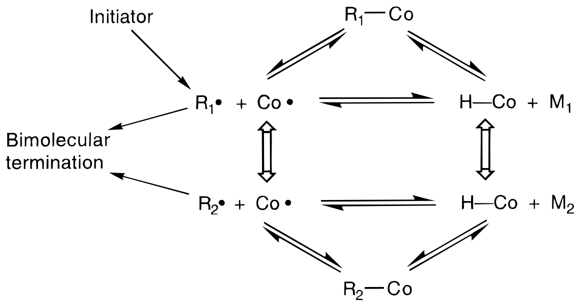
[13] While it is known that the primary reaction observed for the cyanoisopropyl radicals employed in this study is dimerization, this will be relatively unimportant to the overall reaction scheme when a cobalt complex is introduced.[12]

[14] Gridnev, A. A.; Ittel, S. D. To be submitted for publication in *Macromolecules*.

[15] Gridnev, A. A.; Ittel, S. D.; Wayland, B. B.; Fryd, M. Submitted for publication in *Organometallics*.

Scheme 2



the equations. Therefore, from this point on, we will ignore the intermediacy of caged radical pairs of any species.

These effects can be important under conditions of higher solution viscosity or larger, slowly diffusing molecules—the situation often encountered under the conditions of catalytic chain transfer. More importantly, these properties are changing over the course of the reaction as conversion of the monomer goes to completion. As the oligomer or polymer chains become longer, they are subject to increasing diffusional barriers. Under commercially attractive conditions of high monomer or polymer concentrations, the viscosity of the solvent (which may also be monomer under bulk polymerization conditions) is also increased dramatically as the molecular weight builds. This is the cause of the Trommsdorff effect[16] in MMA polymerizations, but it should be noted that the presence of cobalt chain transfer catalysts delays or prevents the onset of Trommsdorff conditions.[2c,6c,17] This must be borne in mind when applying the observations here to CTC.

The reactions connecting the three corners of the triangle in Scheme 1 are all reversible. In fact, the system is overdescribed by the six transformations. It is unlikely that all three pairs of reactions are operable for a given set of reactants and conditions. However, because we cannot reject *a priori* any one pair of the reactions, we will continue to include all of them in the description below.

To this point, we have been simplifying the description to be employed in the remainder of this paper. However, it is our intent to describe the relative reactivities of two dissimilar monomers. Therefore, we have resorted to Scheme 2 to describe the system. The bottom half or the top half would adequately describe a single monomer, but note that there are tie-points or commonalities between the two chemical systems. The concentrations of cobalt(II) and hydridocobalt(III) are common to the two systems. In addition, the concentrations of the radical species are not independent because they are subject to both homo- and cross-bimolecular terminations. A single source of radical is being employed, so the radical R_1 is the only one being supplied externally to the system.

The chemical pathways in Scheme 2 lead to the set of kinetic equations shown in Scheme 3. Again it is acknowledged that the equations in Scheme 3 overdefine the system. It is possible to achieve the same conclusions using a reduced set. The derivations based upon that set are less cumbersome than those included in this paper. Nonetheless, we have maintained the complete set and it will be seen where particular equations are no longer required.

Scheme 3

$$\mathrm{In} \rightarrow 2\mathrm{R}_1 \tag{1}$$

$$\mathrm{R}_1 + \mathrm{R}_1 \xrightarrow{k_{\mathrm{T1}}} \text{non-radical products} \tag{2}$$

$$\mathrm{R}_1 + \mathrm{R}_2 \xrightarrow{k_{\mathrm{TX}}} \text{non-radical products} \tag{3}$$

$$\mathrm{R}_2 + \mathrm{R}_2 \xrightarrow{k_{\mathrm{T2}}} \text{non-radical products} \tag{4}$$

$$\mathrm{R}_1 + \mathrm{Co} \xrightleftharpoons[k_{-1}]{k_1} \mathrm{Co{-}R}_1 \tag{5}$$

$$\mathrm{R}_2 + \mathrm{Co} \xrightleftharpoons[k_{-2}]{k_2} \mathrm{Co{-}R}_2 \tag{6}$$

$$\mathrm{R}_1 + \mathrm{Co} \xrightleftharpoons[k_{-\mathrm{A1}}]{k_{\mathrm{A1}}} \mathrm{Co{-}H} + \mathrm{M}_1 \tag{7}$$

$$\mathrm{R}_2 + \mathrm{Co} \xrightleftharpoons[k_{-\mathrm{A2}}]{k_{\mathrm{A2}}} \mathrm{Co{-}H} + \mathrm{M}_2 \tag{8}$$

$$\mathrm{Co{-}R}_1 \xrightleftharpoons[k_{-\mathrm{B1}}]{k_{\mathrm{B1}}} \mathrm{Co{-}H} + \mathrm{M}_1 \tag{9}$$

$$\mathrm{Co{-}R}_2 \xrightleftharpoons[k_{-\mathrm{B2}}]{k_{\mathrm{B2}}} \mathrm{Co{-}H} + \mathrm{M}_2 \tag{10}$$

In Scheme 3, “In” is an azo initiator which generates the tertiary radical R_1, and M_1 is the monomer obtained after hydrogen abstraction from R_1. M_2 is a second monomer or olefin added to the reaction mixture, and R_2 is the radical formed from monomer M_2 by addition of a hydrogen atom. Co is the cobalt(II) complex (TAP)Co (**3**), and Co−R_1 and Co−R_2 are organocobalt(III) porphyrins, obtained from formal addition of R_1 and R_2, respectively, to **3**. In general, R_1 will be the cyanoisopropyl radical **4**, so the product of addition of R_1, Co−R_1, will be **1**. Formal addition of other radicals, R_2, gives the products Co−R_2 (**2-R**), where R will be specified. Co−H is the hydridocobalt(III) complex (TAP)CoH (**5**).

To the best of our knowledge, there has been little investigation of the reaction of CoH with monomers in cobalt porphyrin systems and the role of cobalt alkyls or the role of the reaction of cobalt(II) species with radical species is poorly understood. In vitamin-B_{12} chemistry, the concept of CoH formation by β-hydrogen abstraction in the radical pair resulting from homolysis of the Co−R bond (reactions 7 and 8) rather than by β-hydrogen elimination (eqs 9 and 10) is the generally accepted pathway.[18] By microscopic reversibility, both the forward and reverse of reactions 7 and 8 must be considered, though there is some evidence that the lifetime of the radical pair is limited.[19] This uncertainty in the CoH chemistry compelled us to compose the most general reaction scheme (Scheme 3, eqs 1−10) with all

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[16] (a) *Encyclopedia of Polymer Science and Engineering*; Wiley: New York, 1987; Vol. 7, 514. (b) Bamford, C. H.; Barb, A. D.; Jenkins, A. D.; Onion, P. F. *The Kinetics of Vinyl Polymerization by Radical Mechanism*; Butterworths: London, 1958. (c) Trommsdorff, E.; Kohle, H.; Lagally, P. *Makromol. Chem.* **1948**, *1*, 169. (d) Stickler, M. *Makromol. Chem.* **1983**, *184*, 2563.

[17] (a) Golikov, I. V.; Mironichev, V. E.; Golubchikov, O. A.; Smirnov, B. R. *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.* **1983**, *26*, 1118; *Chem. Abstr.* **1984**, *100*(10), 68782v. (b) Golikov, I. V.; Semiannikov, V. A.; Mogilevich, M. M. *Vysokomol. Soedin., Ser. B* **1985,** *B27*, 304; *Chem. Abstr.* **1985**, *103*(10), 72735z.

possible reaction pathways. We have chosen to ignore the question of caged radical pairs versus free radicals, believing this to be a fine point better left to further studies.[20]

In the reactions reported above, it was possible to observe steady-state concentrations of the alkylcobalt species for both the cyanoisopropyl Co(III) complex by itself or simultaneously with the respective alkyl complex from 1-hexene, cyclohexene, or cyclopentene. For the steady-state conditions, we can write

$$\frac{d[\mathrm{CoR_1}]}{dt} = k_1[\mathrm{Co}][\mathrm{R_1}] - k_{-1}[\mathrm{CoR_1}] + k_{-\mathrm{B1}}[\mathrm{CoH}][\mathrm{M_1}] - k_{\mathrm{B1}}[\mathrm{CoR_1}] \approx 0 \quad (11)$$

$$\frac{d[\mathrm{CoR_2}]}{dt} = k_2[\mathrm{Co}][\mathrm{R_2}] - k_{-2}[\mathrm{CoR_2}] + k_{-\mathrm{B2}}[\mathrm{CoH}][\mathrm{M_2}] - k_{\mathrm{B2}}[\mathrm{CoR_2}] \approx 0 \quad (12)$$

Equations 11 and 12 can be rewritten:

$$\frac{[\mathrm{CoR_1}]}{[\mathrm{Co}]} = \frac{k_1[\mathrm{R_1}]}{k_{-1} + k_{\mathrm{B1}}} + \frac{k_{-\mathrm{B1}}[\mathrm{CoH}]}{k_{-1} + k_{\mathrm{B1}}}\frac{[\mathrm{M_1}]}{[\mathrm{Co}]} \quad (13)$$

$$\frac{[\mathrm{CoR_2}]}{[\mathrm{Co}]} = \frac{k_2[\mathrm{R_2}]}{k_{-2} + k_{\mathrm{B2}}} + \frac{k_{-\mathrm{B2}}[\mathrm{CoH}]}{k_{-2} + k_{\mathrm{B2}}}\frac{[\mathrm{M_2}]}{[\mathrm{Co}]} \quad (14)$$

At steady state, variations in the concentrations of the cobalt hydride are given by

$$\frac{d[\mathrm{CoH}]}{dt} = k_{\mathrm{A1}}[\mathrm{Co}][\mathrm{R_1}] - k_{-\mathrm{A1}}[\mathrm{CoH}][\mathrm{M_1}] + k_{\mathrm{A2}}[\mathrm{Co}][\mathrm{R_2}] - k_{-\mathrm{A2}}[\mathrm{CoH}][\mathrm{M_2}] + k_{\mathrm{B1}}[\mathrm{CoR_1}] - k_{-\mathrm{B1}}[\mathrm{CoH}][\mathrm{M_1}] + k_{\mathrm{B2}}[\mathrm{CoR_2}] - k_{-\mathrm{B2}}[\mathrm{CoH}][\mathrm{M_2}] \approx 0 \quad (15)$$

so that the steady-state concentration of cobalt hydride is given by

$$[\mathrm{CoH}] = \frac{k_{\mathrm{A1}}[\mathrm{Co}][\mathrm{R_1}] + k_{\mathrm{A2}}[\mathrm{Co}][\mathrm{R_2}] + k_{\mathrm{B1}}[\mathrm{CoR_1}] + k_{\mathrm{B2}}[\mathrm{CoR_2}]}{(k_{-\mathrm{A1}} + k_{-\mathrm{B1}})[\mathrm{M_1}] + (k_{-\mathrm{A2}} + k_{-\mathrm{B2}})[\mathrm{M_2}]} \quad (16)$$

For the steady-state concentration of both radicals in the solution, we have

$$\frac{d[\mathrm{R_1}]}{dt} = V - 2k_{\mathrm{T1}}[\mathrm{R_1}]^2 - k_{\mathrm{TX}}[\mathrm{R_1}][\mathrm{R_2}] - k_1[\mathrm{R_1}][\mathrm{Co}] + k_{-1}[\mathrm{CoR_1}] - k_{\mathrm{A1}}[\mathrm{R_1}][\mathrm{Co}] + k_{-\mathrm{A1}}[\mathrm{CoH}][\mathrm{M_1}] \approx 0 \quad (17)$$

where V is defined as the rate of free radical production, and

$$\frac{d[\mathrm{R_2}]}{dt} = -2k_{\mathrm{T2}}[\mathrm{R_2}]^2 - k_{\mathrm{TX}}[\mathrm{R_1}][\mathrm{R_2}] - k_2[\mathrm{R_2}][\mathrm{Co}] + k_{-2}[\mathrm{CoR_2}] - k_{\mathrm{A2}}[\mathrm{R_2}][\mathrm{Co}] + k_{-\mathrm{A2}}[\mathrm{CoH}][\mathrm{M_2}] \approx 0 \quad (18)$$

Modifying eqs 17 and 18 by adding eqs 11 and 12 and then eq 15 gives

$$V - 2k_{\mathrm{T1}}[\mathrm{R_1}]^2 - 2k_{\mathrm{T2}}[\mathrm{R_2}]^2 - 2k_{\mathrm{TX}}[\mathrm{R_1}][\mathrm{R_2}] = 0 \quad (19)$$

One may assume that $k_{\mathrm{T1}} \approx k_{\mathrm{TX}} \approx k_{\mathrm{T2}}$ because all three are diffusion-controlled and the sizes of the radicals are comparable.[12a] Equation 19 then yields $V = 2k_{\mathrm{T1}}([\mathrm{R_1}] + [\mathrm{R_2}])$. On the other hand, $V = 2k_{\mathrm{T1}}[\mathrm{R_1}]_0^2$, where $[\mathrm{R_1}]_0$ is the concentration of radicals $\mathrm{R_1}$ in a system unperturbed by the addition of porphyrin and monomer. Hence, the sum of concentrations of both radicals

$$[\mathrm{R_1}] + [\mathrm{R_2}] = [\mathrm{R_1}]_0 \quad (20)$$

should be essentially constant, depending only on the rate of initiation. Returning to eq 17, it is evident that $V - 2k_{\mathrm{T1}}[\mathrm{R_1}]^2 - k_{\mathrm{TX}}[\mathrm{R_1}][\mathrm{R_2}] < V$, but

$$V = 2k_{\mathrm{T1}}[\mathrm{R_1}]_0^{\,2} \ll k_1[\mathrm{R_1}][\mathrm{Co}] \quad (21)$$

because k_{T1} and k_1 have very similar values. Because $[\mathrm{R_1}]_0$ is several orders of magnitude less than [Co]

$$k_1[\mathrm{R_1}][\mathrm{Co}] + k_{\mathrm{A1}}[\mathrm{R_1}][\mathrm{Co}] \approx k_{-1}[\mathrm{CoR_1}] + k_{-\mathrm{A1}}[\mathrm{CoH}][\mathrm{M_1}]$$

Equation 18 can be simplified similarly, allowing the concentrations of $\mathrm{R_1}$ and $\mathrm{R_2}$ to be estimated by eqs 22 and 23.

$$[\mathrm{R_1}] = \frac{k_{-1}[\mathrm{CoR_1}] + k_{-\mathrm{A1}}[\mathrm{CoH}][\mathrm{M_1}]}{(k_1 + k_{\mathrm{A1}})[\mathrm{Co}]} \quad (22)$$

$$[\mathrm{R_2}] = \frac{k_{-2}[\mathrm{CoR_2}] + k_{-\mathrm{A2}}[\mathrm{CoH}][\mathrm{M_2}]}{(k_2 + k_{\mathrm{A2}})[\mathrm{Co}]} \quad (23)$$

If

$$k_{-1}[\mathrm{CoR_1}] \gg k_{-\mathrm{A1}}[\mathrm{CoH}][\mathrm{M_1}]$$

and

$$k_{-2}[\mathrm{CoR_2}] \gg k_{-\mathrm{A2}}[\mathrm{CoH}][\mathrm{M_2}]$$

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(18) (a) Halpern, J. *Science (Washington, D.C.)* **1985**, *227*, 869. ((b) Garr, C. D.; Finke, R. G. *J. Am. Chem. Soc.* **1992**, *114*, 10440. (c) Sweany, R. L.; Halpern, J. *J. Am. Chem. Soc.* **1977**, *99*, 8335. (d) Gjerde, M. D.; Espenson, J. H. *Organometallics* **1982**, *1*, 435. (e) Garr, C. D.; Finke, R. G. *Inorg. Chem.* **1993**, *32*, 4414. (f) Ng, F. T. T.; Rempel, G. L.; Mancusto, C.; Halpern, J. *Organometallics* **1990**, *9*, 2762. (g) Gridnev, A. A.; Semeikin, A. S.; Koifman, O. I. *Teor. Eks. Khim.* **1990**, *26*, 128; *Theor. Exp. Chem. (Engl. Transl.)* **1990**, *26*, 118.

(19) The intermediacy of a caged radical pair of an appreciable lifetime would seem to be contradicted by our observation of up to 90% stereoselectivity in the addition of CoH to the double bond of a cyclic olefin or to the triple bond of an acetylene. If the reaction CoH + M goes through $\{(\mathrm{Co^{III}})^{\bullet} + {}^{\bullet}\mathrm{R}\}$ radical pair formation followed by recombination to yield CoR, stereospecificity limits the lifetime of the caged radical pair to a time comparable to the time required for a single rotation of the radical in the radical cage before addition or 10^{-10} s. Gaudener et al. also found only moderate stereoselectivity (~65%) in the addition of olefins to hydridocobaloximes: Derenne, S.; Gaudemer, A.; Johnson, M. D. *J. Orgamomet. Chem.* **1987**, 322, 2291.

(20) Cage effects have been demonstrated to play an important role in a number of organometallic systems noted below, but in this particular study, all of the work was done in a single, low-viscosity medium. We do not believe cage effects to have played a role in the observations reported here. See, for instance, ref 13e and: (a) Koenig, T.; Fischer, H. In *Free Radicals;* Kochi, J., Ed.; Wiley: New York, 1973; Vol. 1. (b) Gerards, L. E. H.; Bulthuis, H.; de Bolster, M. W. G.; Balt, S. *Inorg. Chim. Acta* **1991**, *190*, 47. (c) Bagdasar'yan, Kh. S. *Usp. Khim.* **1984**, *53*, 1073; *Russ. Chem. Rev. (Engl. Transl.)* **1984**, *53*, 1100. (d) Koenig, T. W.; Finke, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 2657. (e) Kim, S.-H.; Chen, H. L.; Feilchenfeld, N.; Halpern, J. *J. Am. Chem. Soc.* **1988**, *110*, 3120.

we obtain

$$\frac{[R_1]}{[R_2]} = \frac{(k_2 + k_{A2})k_{-1}}{(k_1 + k_{A1})k_{-2}} \frac{[CoR_1]}{[CoR_2]} \tag{24}$$

In the alternative case, when $k_{-1}[CoR_1] \ll k_{-A1}[CoH][M_1]$, the ratio between the concentrations of the two radicals given in eqs 22 and 23 may be reduced to

$$\frac{[R_1]}{[R_2]} = \frac{(k_2 + k_{A2})k_{-A1}}{(k_1 + k_{A1})k_{-A2}} \frac{[M_1]}{[M_2]} \tag{25}$$

Equations 24 and 25 reflect on the issue of whether the free radicals in solution are formed primarily by homolysis of the Co–C bond of the organocobalt porphyrin complexes (the reverse direction in reactions 5 and 6) or by reaction of hydridocobalt porphyrin with monomers (pathways 7 and 8).

In eqs 24 and 25, $k_2 > k_{A2}$ and $k_1 > k_{A1}$ because reactions 5 and 6 are radical–radical combinations and are therefore "activationless" but reactions 7 and 8 would be expected to have activation energies. Hence, if organocobalt porphyrin CoR_1 is less stable than complex CoR_2 ($K_2 \gg K_1$), then under the conditions of eq 24

$$\frac{[R_1]}{[R_2]} \gg 1 \tag{26}$$

and conversely, if CoR_2 is less stable, then

$$\frac{[R_1]}{[R_2]} \ll 1 \tag{27}$$

Comparison of eqs 26 and 27 with eq 20 indicates that the partial concentrations of the radicals of each type depend on the stability of the corresponding organocobalt porphyrin. Analogously, consideration of eq 25 leads to the conclusion that the concentration of the particular radical depends on the rate of reaction of CoH with the corresponding monomer. It is not crucial by which mechanism ((5)–(6) or (7)–(8)) the cobalt porphyrin liberates free radicals into the solution; the important factor is that the relationship between the concentrations of the two radicals is independent of the rate of initiation by azo initiator.

Another conclusion is that the type and concentration of the azo initiator influences only the total concentration of free radicals in the system. The role of the azo initiator at steady state during synthesis is, therefore, simply to compensate for the loss of free radicals by normal termination reactions. Condition 21 illustrates this issue. The available free radicals at steady state are generated primarily by homolysis of CoR or by reaction of CoH with available monomers by the reverse of reactions 5–8. Those radicals react more rapidly with $(Co^{II})^{\bullet}$ than with other radicals simply because the $(Co^{II})^{\bullet}$ is available in much higher concentrations. This is characteristic of systems containing persistent radicals.[21] The loss of some of those free radicals by normal recombination or disproportionation reactions is compensated for by generation from the azo initiator.

If CoH is formed primarily by β-hydrogen abstraction from the radical, rather than by β-hydride elimination from alkylcobalt(III) as is commonly accepted,[17] then

$$k_{A1}[R_1][Co] + k_{A2}[R_2][Co] \gg k_{B1}[CoR_1] + k_{B2}[CoR_2] \tag{28}$$

so that eq 16 reduces to

$$[CoH] = \frac{k_{A1}[R_1] + k_{A2}[R_2]}{(k_{-A1} + k_{-B1})[M_1] + (k_{-A2} + k_{-B2})[M_2]}[Co] \tag{29}$$

According to eq 17, neglecting $V - k_{T1}[R_1]^2 - k_{TX}[R_1][R_2]$ relative to $k_1[R_1][Co]$, we have

$$[R_1] = \frac{k_{-1}[CoR_1]}{(k_1 + k_{A1})[Co]} + \frac{k_{-A1}[CoH][M_1]}{(k_1 + k_{A1})[Co]} \tag{30}$$

If we substitute (30) and (29) into eq 13

$$\frac{[CoR_1]}{[Co]} = K_{R1}\frac{k_{A1}[R_1] + k_{A2}[R_2]}{(k_{-A1} + k_{-B1})[M_1] + (k_{-A2} + k_{-B2})[M_2]}[M_1] \tag{31}$$

where

$$K_{R1} = \frac{k_{-A1}k_1 + k_{-B1}k_1 + k_{-B1}k_{A1}}{k_1k_{B1} + k_{A1}k_{-1} + k_{A1}k_{B1}}$$

Similarly, if we apply eqs 14, 18, and 29, then

$$\frac{[CoR_2]}{[Co]} = K_{R2}\frac{k_{A1}[R_1] + k_{A2}[R_2]}{(k_{-A1} + k_{-B1})[M_1] + (k_{-A2} + k_{-B2})[M_2]}[M_2] \tag{32}$$

for the partial concentration of the second organometallic, where

$$K_{R2} = \frac{k_{-A2}k_2 + k_{-B2}k_2 + k_{-B2}k_{A2}}{k_2k_{B2} + k_{A2}k_{-2} + k_{A2}k_{B2}}$$

The condition

$$(k_{-A1} + k_{-B1})[M_1] \gg (k_{-A2} + k_{-B2})[M_2] \tag{33}$$

occurs when monomer M_1 reacts with CoH faster than does monomer M_2. In this case, eqs 31 and 32 give eqs 34 and 35:

$$\frac{[CoR_1]}{[Co]} = K_{R1}\frac{k_{A1}[R_1] + k_{A2}[R_2]}{k_{-A1} + k_{-B1}} \tag{34}$$

$$\frac{[CoR_2]}{[Co]} = K_{R2}\frac{k_{A1}[R_1] + k_{A2}[R_2]}{k_{-A1} + k_{-B1}}\frac{[M_2]}{[M_1]} \tag{35}$$

The monomer M_1, which reacts faster than M_2, produces the organocobalt chelate CoR_1, whose relative concentration at steady state does not depend on the concentration of both monomers M_1 and M_2 but depends linearly on the total concentration of free radicals. These are the conditions illustrated in Figures 2 and 4.

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[21] (a) Fisher, H. *J. Am. Chem. Soc.* **1986**, *108*, 3925. (b) Daikh, B. E.; Finke, R. G. *J. Am. Chem. Soc.* **1992**, *114*, 2938.

Similarly, for the conditions

$$(k_{-A1} + k_{-B1})[M_1] \ll (k_{-A2} + k_{-B2})[M_2]$$

the very same dependencies are obtained:

$$\frac{[CoR_1]}{[Co]} = K_{R1}\frac{k_{A1}[R_1] + k_{A2}[R_2]}{k_{-A2} + k_{-B2}}\frac{[M_1]}{[M_2]}$$

$$\frac{[CoR_2]}{[Co]} = K_{R2}\frac{k_{A1}[R_1] + k_{A2}[R_2]}{k_{-A2} + k_{-B2}}$$

The only difference from eqs 34 and 35 is that now $[CoR_2]/[Co]$ does not depend on the concentrations of the monomers. There is no significant difference in behavior between M_1 and M_2, or between R_1 and R_2. The experimental observation depends only upon whether M_1 or M_2 is more active in the reaction with CoH. It does not matter whether one of the monomers is derived from the initiator. The significance of this is that the role of initiating radicals is simply to supply the system with CoH, confirming the conclusion made below eq 27. The nature of the radical does not matter so long as it can supply a hydrogen atom to Co(II).

In the system where only AIBN and MAN are added to the reaction mixture (therefore, $[R_2] = [M_2] = 0$), by eq 31 we would have

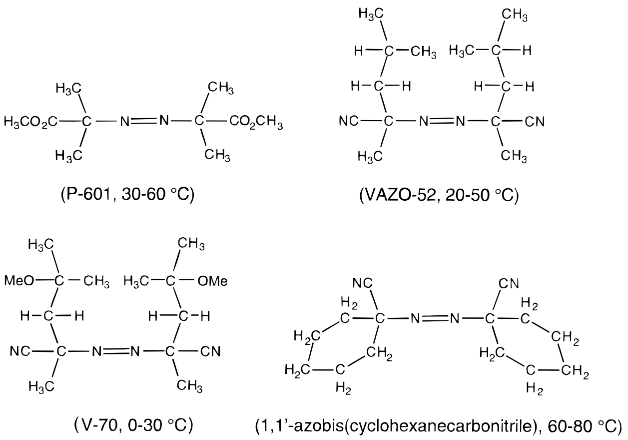
$$\frac{[CoR_1]}{[Co]} = \frac{k_1 + \mu k_{A1}}{k_{-1} + k_{B1}\left(1 + \frac{k_1}{k_{A1}}\right)}[R_1] \qquad (36)$$

where

$$\mu = \frac{k_{-B1}}{k_{-A1} + k_{-B1}} \leq 1$$

Above, it has been pointed out that k_1 should be much greater than k_{A1} and, therefore, $k_1 \gg \mu k_{A1}$. In our previous work, we found that (TAP)Co–OO–C$(CH_3)_2$-CN is rapidly formed upon exposure of **1** to air at 23 °C. This product is presumably formed by dissociation of the radical, where it traps oxygen to form the peroxy radical, which recombines with Co(II).[9b] Because it is difficult to suggest a reasonable mechanism involving the intermediacy of a hydridocobalt complex and a monomer, this suggests that, at room temperature, Co–C bond homolysis dominates β-hydrogen elimination by reaction 9 (i.e. $k_{-1} \gg k_{B1}$). Additional evidence can be found by comparison of k_{T1} for polymeric MMA radicals, and the rate constant of catalytic chain transfer, k_s, in radical polymerization with reaction I is a rate-limiting step. According to published data, $k_{T1} \approx 2 \times 10^7$ M^{-1} s^{-1},[22] while for the cobalt porphyrin $k_s \approx 10^6$ M^{-1} s^{-1} [23] or $k_s \approx 0.1k_{T1}$. In our case k_s would be the same as k_{B1}.

Chart 1


(P-601, 30-60 °C)
(VAZO-52, 20-50 °C)
(V-70, 0-30 °C)
(1,1′-azobis(cyclohexanecarbonitrile), 60-80 °C)

The denominator of eq 36 can be simplified if

$$k_{-1} \gg k_{B1}\frac{k_1}{k_{A1}} \qquad (37)$$

The inequality in (37) can be rewritten as

$$K_1 \ll \frac{k_{A1}}{k_{B1}} \quad \text{or} \quad \frac{k_{A1}}{k_1} \gg \frac{k_{B1}}{k_{-1}} \qquad (38)$$

The condition expressed in (38) means that β-hydrogen elimination from the organocobalt derivative (forward of reaction 9) should be much slower than Co–C bond homolysis (reverse of reaction 5), and the formation of cobalt hydride by reaction 7 should be relatively facile.

If condition 38 is applicable to the system, we can transform eq 36 into eq 39 without a significant error.

$$\frac{[CoR_1]}{[Co][R_1]} = \frac{k_1}{k_{-1}} = K_1 = \frac{[CoR_1]}{[Co]}\sqrt{\frac{2k_{T1}}{V}} \qquad (39)$$

Equation 39 allows the determination of the temperature dependence of the equilibrium constant, K_1. AIBN does not generate an adequate flux of radicals over a sufficiently wide range of temperature to adequately determine equilibrium constants K_1 for a thermodynamic determination. Recalling the conclusion that the role of initiating radicals is simply to supply the system with CoH, lower temperature azo initiators have been utilized as sources of CoH. The initiators shown in Chart 1 produce no organocobalt porphyrin complexes when used alone due to the increased steric demands of the resulting alkyl groups, but in the presence of methacrylonitrile, there is immediate formation of (TAP)Co–C$(CH_3)_2$CN. Using MAN as M_1, $(CH_3)_2(CN)$-$C^{\bullet}$ as R_1, and any of the above resulting initiating radicals as R_2 in eq 32, we obtain an equation similar to eq 38 to determine the value of the equilibrium constants for **1** when $[R_1] \gg [R_2]$. On the other hand, if $[R_1] \ll [R_2]$ we would have

$$\frac{[CoR_1]}{[Co][R_2]} = K_1\frac{k_{A2}}{k_{A1}} \qquad (40)$$

Although $[R_2]$ could be equal to $[R_1]$ in the previous case (see eq 20), the right side of eq 40 differs from that in eq 39. Equations 39 and 40 give the same value of

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[22] (a) O'Brien, J. L.; Gormick, F. *J. Am. Chem. Soc.* **1955**, *77*, 4757. (b) Schulz, G. V.; Henrici-Olive, G.; Olive, S. *Z. Phys. Chem. (Frankfurt)* **1960**, *27*, 1.

[23] Mironichev, V. Ye.; Mogilevich, M. M.; Smirnov, B. R.; Shapiro, Yu. Ye.; Golikov, I. V. *Vysokomol. Soedin.* **1986**, *A28*, 1891; *Polym. Sci. U.S.S.R.* **1986**, *28*, 2103.

the equilibrium constant only if the equilibrium constants for reactions 7 and 8, k_{A1} and k_{A2}, are the same. Therefore, if the concentration of radicals R_2 is comparable to or larger than the concentration of R_1, determination of K_1 with AIBN as a source of free radicals should give a value for this constant which is different from those obtained by applying other azo initiators. Table 1 gives very similar values of K_1 for (TAP)Co$-$C$(CH_3)_2$CN on employing three different azo initiators at 23 °C, thereby indicating that $[R_1] \gg [R_2]$ (or that $k_{A1} = k_{A2}$ which seems unlikely). Thus, the tertiary radicals shown above do not form stable organometallic species but are quite adequate as hydrogen atom donors to convert Co^{II} to $Co^{III}H$.

According to Table 1, at 60 °C for methacrylonitrile (as M_1), K_1, which is defined by k_1/k_{-1}, is 4.3×10^6. As indicated above, $k_1 \leq k_{T1}$. Therefore, the dissociation rate constant for **1** at this temperature is $k_{-1} = k_1/K_1 \leq k_{T1}/K_1 = (1.3 \times 10^9)/(4.3 \times 10^6)$ or $\sim 300\ s^{-1}$.

The situation changes when monomers which form secondary radicals are added to the reaction mixture. These radicals (R_2) would give CoR_2 products significantly more stable than (TAP)Co$-$C$(CH_3)_2$CN (CoR_1). Applying assumption 41

$$[R_1] \gg [R_2] \text{ and } k_{A1}[R_1] \gg k_{A2}[R_2] \tag{41}$$

we can reduce eqs 34 and 35 to eqs 42 and 43.

$$\frac{[CoR_1]}{[Co]} = \text{const}_1[R_1] \approx K_1[R_1] \tag{42}$$

$$\frac{[CoR_2]}{[Co]} = \text{const}_2[R_1]\frac{[M_2]}{[M_1]} \tag{43}$$

where

$$\text{const}_2 = K_2\frac{k_{A1}}{k_{A2}}\frac{k_{-A2} + k_{-B2}}{k_{-A1} + k_{-B1}} \tag{44}$$

The observed dependence of the concentrations of organometallics **2** and **1** on the concentration of initiators (Figure 7) shows that the ratio [CoR]/[Co] increases linearly with the concentration of radicals as predicted by eqs 42 and 43. According to eq 42, addition of an aliphatic alkene M_2 should not change the value of the equilibrium constant, K_1, for **1**. Utilizing the data of Figure 7, the calculated value of K_1 for organometallic **1** in the presence of added cyclohexene clearly coincides with those obtained in the absence of cyclohexene (Figure 8). Hence, by eq 20, the concentration of radicals R_2 must be very small, confirming assumption 41.

Additional insight can be obtained by varying the relative concentrations of the two monomers. The data in Figure 9 (cyclopentene as M_2 and MAN as M_1) show that the ratio $[CoR_1]/[Co]$ is independent of the ratio $[M_2]/[M_1]$, but the value of $[CoR_2]/[Co]$ decreases linearly with $[M_2]/[M_1]$. The slope of the line gives constant$_2$-$[R_1] = 4 \times 10^{-3}$. When data from Table 1 and eqs 19 and 20 are applied, the concentration $[R_1]$ was found to be 2×10^{-8} M. Therefore, constant$_2 = 2 \times 10^5\ M^{-1}$. For $LCoR_2$ which is more stable than $LCoR_1$, it should be $K_2 \ll K_1 = 4.3 \times 10^6$. We believe that k_{A1} should not differ greatly from k_{A2}. Furthermore, k_{A1} should be larger than k_{A2} because radical **4** is smaller than the other radicals and it has two methyl groups suitable for hydrogen abstraction. Then, $(k_{-A2} + k_{-B2})/(k_{-A1} + k_{-B1}) \ll 4 \times 10^{-2}$. In other words, LCoH reacts with monomer M_1 at least 25 times faster than monomer M_2 under the conditions of Figure 9. This number matches other estimates of $(k_{-A2} + k_{-B2})/(k_{-A1} + k_{-B1})$. We see in Figure 9 that $[CoR_2]/[Co]$ is linearly dependent on the ratio between the concentrations of the monomers to values of [cyclopentene]/[MAN] approaching 400.[24] Therefore, $(k_{-A2} + k_{-B2})/(k_{-A1} + k_{-B1}) \leq 5 \times 10^{-3}$; thus, at this level of approximation, the data are consistent.

Increasing the ratio $[M_2]/[M_1]$, we move the system into a situation where

$$[R_1] \approx [R_2] \text{ and } k_{A1}[R_1] \approx k_{A2}[R_2] \tag{45}$$

When the concentrations of both radicals (R_1 and R_2) are comparable, the analysis of the behavior of [CoR]/[Co] becomes complex for individual radicals. The situation is simplified by dividing eq 31 by eq 32, yielding eq 46. Equation 46 reflects the mutual dependence of the partial concentrations of both organometallics in the reaction system. This equation indicates that the left side of (46) should be a constant, specific to any pair of monomers or their respective radicals regardless of the reaction pathways which dominate their formation. Only when there is knowledge of the predominate pathway for CoH formation and its reactions with M_1 and M_2 can there be further simplification of eq 46 to evaluate specific rate constants.

$$\frac{[CoR_1]}{[CoR_2]}\frac{[M_2]}{[M_1]} = \frac{K_{R1}}{K_{R2}} \tag{46}$$

For example, if the dominant reaction of CoH with a monomer is to produce the Co(III) organometallics rather than Co(II) and the organic radical ($k_{-A1} \ll k_{-B1}$ and $k_{-A2} \ll k_{-B2}$), then eq 46 would be reduced to eq 47

$$\frac{[CoR_1]}{[CoR_2]}\frac{[M_2]}{[M_1]} = \frac{K_1}{K_2}\frac{k_{-B1}}{k_{A1}}\frac{k_{A2}}{k_{-B2}} \tag{47}$$

if $k_{A1}/k_{B1} \gg K_1$ and $k_{A2}/k_{B2} \gg K_2$. Under these circumstances, the formation of CoH by Co(II) abstraction of a hydrogen atom from a radical (eq 7) is preferred over β-hydride elimination from the alkylcobalt(III) species (eq 9). This condition is reflected in the initial simplifying assumption (28), and therefore, eq 47 is not contradicted by the assumptions from which it was derived. Returning to kinetic Scheme 3, we see that eq 47 can be applied to the system when most of the CoH is produced by the reaction of free radicals with cobalt(II). However, the reverse reaction re-forms CoH at a very high rate.

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[24] It is necessary to explain that the point [cyclopentene]/[MAN] = 380 in Figure 9 was obtained without the direct addition of MAN to the reaction solution. Some MAN forms during *tertiary radical synthesis* whenever AIBN is used as source of tertiary radicals through reaction V. Moreover, the concentration of MAN should be equal to that of $LCoR_2$. Using the observed concentration of LCo$-$cyclopentyl (0.0052 M) as the concentration of MAN, the value [cyclopentene]/[MAN] = 380 has been calculated. It is in reasonable agreement with the remainder of the points obtained by direct addition of MAN to the reaction, thereby indicating the very rapid reaction of MAN with the hydridocobalt porphyrin complex. The point appears to be low, but the considerable error in this particular measurement makes any attempt at explanation difficult.

If $k_{-A1} \gg k_{-B1}$ and $k_{-A2} \gg k_{-B2}$, this together with assumption 28 would indicate that equilibria 7 and 8 are more important than equilibria 9 and 10. The relationship

$$\frac{[\mathrm{CoR}_1]}{[\mathrm{CoR}_2]}\frac{[\mathrm{M}_2]}{[\mathrm{M}_1]} = \frac{K_1}{K_2}\frac{K_{A2}}{K_{A1}} \tag{48}$$

is derived from a series of parallel equilibrium reactions. If the $[\mathrm{M}_2]/[\mathrm{M}_1]$ ratio is increased further, then

$$[\mathrm{R}_1] \ll [\mathrm{R}_2] \text{ and } k_{A1}[\mathrm{R}_1] \ll k_{A2}[\mathrm{R}_2] \tag{49}$$

Under these conditions, eqs 31 and 32 become eqs 42 and 43 but with the role of the two monomers reversed. This conclusion is important because it indicates the generality of the mechanism. As set out, the mechanism in Scheme 2 relies upon an azo initiator which produces only the first radical species. In our studies, we want to limit the number of species in the system; therefore, we have generally chosen an initiator which produces M_1, but this has no bearing upon the outcome of the overall reactions. As indicated above, many different radicals will suffice and whether the radical is based upon M_1 or M_2 makes no difference in the outcome of the kinetic relationships derived here.

Summary

We have derived a general kinetic model to describe the interaction of two dissimilar olefins with cobalt(II) tetrakis(anisyl)porphyrin in the presence of organic radicals. The scheme presumes the formation of organometallic products both by radical addition to Co(II) and by reaction of hydridocobalt(III) complexes with the corresponding olefins. The proposed general mechanism also presumes that cobalt hydride is formed by two pathways—either by bimolecular reaction of the Co(II) porphyrin complex with the radical or by unimolecular β-hydrogen atom elimination from the organocobalt(III) species.

The general model was then modified to the specific case of competition between methacrylonitrile and aliphatic olefins. When the simplifying assumption is applied that most of the hydride forms through the bimolecular reaction and that both olefins follow the same predominant reaction pathways, a mathematical model of the concentration of organometallic species derived from both olefins was developed. This dependence allows the evaluation of some elementary relative reaction rate constants for dissociation of the Co–C bonds and reactions of the olefins with the hydridocobalt complex.

The model we have proposed is for the general case, and it has been applied to one specific pair of olefins. Consideration of these two olefins of considerably different reactivities allows us to draw a number of conclusions.

(1) Despite the presence of an appreciable concentration of radical species, the chemistry is very dependent upon the relative rates of reaction of the monomers with CoH.

(2) The differences in rates of reactions of olefins with CoH can be employed in strategies for the synthesis of various alkylcobalt(III) species.

(3) Under some conditions, the radicals derived from the initiators serve only to provide the system with hydridocobalt(III), thereby removing the constraint that use of olefins with other than their respective azo initiators will complicate the analysis.

(4) The relative rate constants for the reaction of CoH with various monomers can be obtained in a straightforward manner when the relative concentrations of the two olefins are such that their rates of reaction of CoH are equal.

(5) The dependence of the relative concentration of organometallic compound on the ratio $[\mathrm{M}_1]/[\mathrm{M}_2]$ can be divided into five important regions. When LCoR_1 or LCoR_2 are the only observed organocobalt products in the reaction mixture, the values of the equilibrium constants K_1 and K_2 can be obtained. Under intermediate conditions, relative rate constants for the reaction of CoH with various monomers can be obtained.

(6) The equilibrium constant for homolytic dissociation of the organocobalt Co–C bond can be measured directly when one species is dominating the reaction.

(7) The general scheme described here can be applied to a wide variety of systems, but the relative rates of the various reactions will have to be considered on a case by case basis.

Each of these points will now be dealt with in more detail.

(1) Comparison of the experimental results with the kinetic analysis of cobalt porphyrin chemistry with two different monomers in the presence of free radicals shows that the rate of monomer reaction with hydridocobalt porphyrin is responsible for much of the observed chemistry. Individual rate constants for monomer reactions with CoH are very dependent on the structure and electronics of the monomer and can differ by several orders of magnitude. For instance, methacrylonitrile reacts with CoH much faster than do unfunctionalized alkenes, despite the fact that the organometallic formed by MAN is less stable than that formed by the simple alkene. This lower Co–C bond strength, reflecting both the steric interactions in the relatively crowded complex and the increased stability of the resulting organic radical, is manifested in the rate of Co–C bond homolysis.

(2) Differences in the rates of CoH reaction with monomers can be employed in the synthesis of organocobalt complexes. In a previous paper[9b] we observed that the use of lower temperature together with less stable initiators such as Vazo-52 and V-70 remarkably increased the yield of organometallics relative to those obtained with AIBN. Azo initiators which produce monomers with reduced ability to abstract a hydrogen atom from hydridocobalt complexes (lower k_{-A}) lead to an increase in the yield of organometallics during syntheses employing tertiary radicals as a hydrogen atom source. We hope to better define how this rate constant depends on the structure of the monomer and cobalt chelate in a subsequent paper.

(3) The sole function of some initiators is to provide the system with a source of hydridocobalt(III) or hydrogen atoms. If the olefin formed by H abstraction from the initiator radical reacts slowly with the resulting hydridocobalt(III) complex, then the presence of this monomer can be neglected in kinetic studies. Utilization of such an initiator is thus a convenient tool for

probing the relationship between two other monomers, because this initiator and the monomer it produces have no visible influence on the formation of organometallics by the two additional monomers. The system can still be handled as a two-monomer system exactly as described in this paper. Initiators that fit these criteria generally produce tertiary radicals lacking methyl groups or are very sterically hindered. Initiators which yield radicals such as cyanocyclohexyl or 3-cyano-3-pentyl are good examples.

(4) The relationship between the concentrations of organometallics and the concentration of the monomer can be used to determine the relative rate constants for the reactions of CoH with the monomers. When the relative concentrations of the two monomers are such that the rates of reaction of CoH with both monomers are equal

$$(k_{-\mathrm{A}1} + k_{-\mathrm{B}1})[\mathrm{M}_1] = (k_{-\mathrm{A}2} + k_{-\mathrm{B}2})[\mathrm{M}_2] \qquad (50)$$

then eq 31 gives us eq 51:

$$\frac{[\mathrm{CoR}_1]}{[\mathrm{CoR}_1]_0} = 0.5\frac{[\mathrm{R}_1] + \dfrac{k_{\mathrm{A}2}}{k_{\mathrm{A}1}}[\mathrm{R}_2]}{[\mathrm{R}_1]_0} \qquad (51)$$

$[\mathrm{CoR}_1]_0$ is the concentration of CoR_1 when no M_2 has been introduced to the system. As was shown above, the sum $[\mathrm{R}_1] + [\mathrm{R}_2]$ is approximately equal to $[\mathrm{R}_1]_0$. Therefore, if $k_{\mathrm{A}2} \approx k_{\mathrm{A}1}$, the partial concentration of CoR_1 is half the concentration it would be in the absence of monomer M_2. If $k_{\mathrm{A}2} \gg k_{\mathrm{A}1}$, the situation is more complicated, but the equilibrium concentration of CoR_1 could be close to $[\mathrm{CoR}_1]_0$. If $k_{\mathrm{A}1} \gg k_{\mathrm{A}2}$, the partial concentration of CoR_1 would be 25% of $[\mathrm{CoR}_1]_0$.

Published data on chain transfer catalysis[2a−c,11a,13g] and living radical polymerization[25] indicates that the most efficient abstraction of hydrogen atoms from radical species (the highest $K_{\mathrm{A}2}$) is observed in radicals having a β-methyl group. For instance, methyl methacrylate chain transfer is very efficient, while chain transfer is inefficient for methyl acrylate due to the formation of high concentrations of the alkylcobalt(III) adduct. Therefore, in the case of vinylic monomers such as methyl acrylate which form secondary radicals, a reduction of ≈50% in $[\mathrm{CoR}_1]/[\mathrm{Co}]$ is expected when

$$(k_{-\mathrm{A}1} + k_{-\mathrm{B}1})[\mathrm{M}_1] = (k_{-\mathrm{A}2} + k_{-\mathrm{B}2})[\mathrm{M}_2]$$

and M_1 is a vinylidenic monomer such as methacrylonitrile. Unfortunately, this method cannot distinguish whether reaction −8 or −10 dominates. It cannot be ruled out that the reaction pathways depend on the structure of the radical or the organocobalt chelate or that it would be possible to shift from one to the other mechanism upon changing reaction conditions.

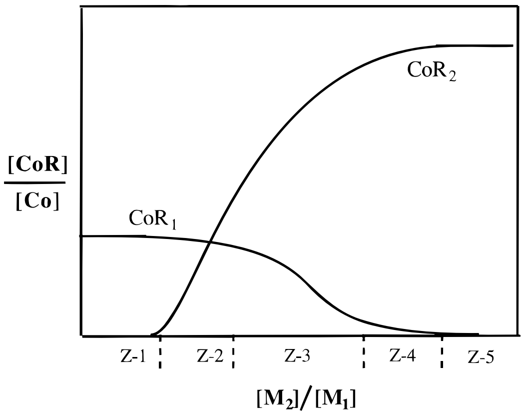
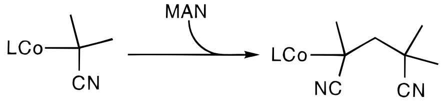


Figure 10. Representation of the dependence of the relative steady-state concentrations of LCoR_1 and LCoR_2 on the ratio of concentrations of olefins in the reaction solution under the conditions given by eqs 31 and 32.

Interestingly, it is possible to estimate $k_{-\mathrm{A}} + k_{-\mathrm{B}}$ for olefins which do not form organocobalt chelates at concentrations observable by NMR through eq 51. With one olefin as a reference, it is possible to obtain data on the relative rate constants for the reaction of the hydridocobalt complex with the other monomer. The best reference compounds would be those which are relatively unstable, forming low but observable concentrations of organocobalt complex, because they would be easily converted into more stable species. Fortuitously, the cyanoisopropyl derivative is a good reference, because it meets these criteria and is readily available from either the monomer or the azo initiator. Another positive feature of this radical is that its six protons appear as a singlet in the NMR spectrum, allowing reasonable quantification even at lower concentrations. Finally, despite the fact that MAN will polymerize, its radical oligomer adduct



(5)

can be ignored because the resulting organometallic product **5** is unstable due to the slight increase in size; it is not an observed organometallic product even at prolonged reaction times.

(5) Valuable information on the relative rate constants of monomers reacting with CoH under a variety of concentration conditions is provided by eqs 31 and 32. The dependence of the relative concentrations of organometallic compound on the ratio $[\mathrm{M}_1]/[\mathrm{M}_2]$ can be divided into five important regimes, illustrated in Figure 10. At the two extreme conditions, indicated by zones Z-1 and Z-5, when either LCoR_1 or LCoR_2 are the only observed organocobalt products in the reaction mixture, the values of the equilibrium constants K_1 and K_2 can be obtained in a straightforward manner because the other monomer can be ignored. Between those extremes, when both organocobalt species can be observed simultaneously but one or the other of them prevail (zones Z-2 and Z-4), information on the values of $k_{-\mathrm{A}1} + k_{-\mathrm{B}1}$ and $k_{-\mathrm{A}2} + k_{-\mathrm{B}2}$ can be obtained as described in conclusion 4. Although this information could obtained for both monomers in either zone, zone Z-2 is more

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[25] (a) Webster, O. W. *Science (Washington, D.C.)* **1991**, *251*, 887. (b) Otsu, T.; Yoshida, M.; Tazaki, T. *Makromol. Chem., Rapid Commun.* **1982**, *3*, 127. (c) Moad, G.; Rizzardo, E.; Solomon, D. H. *Polym. Bull.* **1982**, *6*, 589. (d) Druliner, J. D. *Macromolecules* **1991**, *24*, 6079. (e) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules* **1993**, *26*, 5316. (f) Wayland, B. B.; Poszmik, G.; Mukerjee, S. L.; Fryd, M. *J. Am. Chem. Soc.* **1994**, *116*, 7943. (g) Smirnov, B. R. *Vysokomol. Soedin.* **1990**, *A23*, 583; *Polym. Sci. U.S.S.R.* **1990**, *A23*, 524. (h) Oganova, A. G.; Smirnov, B. R.; Ioffe, N. T.; Enikolopyan, N. S. *Dokl. Akad. Nauk SSSR* **1983**, *268*, 917; *Dokl. Chem. (Transl. of Dokl. Akad. Nauk)* **1983**, 268, 66.

convenient for such measurements because the concentrations of the two organometallics are approximately equal in zone 2. In zone 4, measurement of the concentration of [CoR_1] is less accurate due to low relative concentrations. The values of $k_{-A1} + k_{-B1}$ and $k_{-A2} + k_{-B2}$ obtained from these measurements can be then be used in the calculation of the ratio k_{A1}/k_{A2}, applying the slope of the dependence of [CoR_2]/[Co] according to eqs 43 and 44. Although eq 46 is true for the entire range of concentrations of M_1 and M_2, the intermediate zone Z-3 provides the most accurate measurements of constants K_{R1} and K_{R2} because both of the organometallic species are present in relatively high concentrations. The values of K_{R1} and K_{R2} found in Z-3 can then be used for verification of the measurements of concentrations of the organometallics when they are in their lower levels or for estimation of concentration of organocobalt complexes when they are below detectable limits. For example, eq 46 allows the estimation of the concentration of $LCoR_1$ in Z-4, where [CoR_1] is too low for accurate estimation of the ratio $(k_{-A2} + k_{-B2})/(k_{-A1} + k_{-B1})$. Comparison of the values of $(k_{-A2} + k_{-B2})/(k_{-A1} + k_{-B1})$ measured in Z-2 and Z-4 would provide additional information on k_{A1}/k_{A2}. Ideally, they should agree very closely. Otherwise, the simplifying assumptions should be reconsidered because a shift in the predominate reaction pathways for monomers M_1 or M_2 could be indicated.

Unfortunately, unsubstituted olefins react so slowly with LCoH relative to methacrylonitrile that it is impossible to add enough to overcome the reactivity of MAN. The portion of the kinetic dependence when only $LCoR_2$ can be observed in the reaction mixture has not been achieved. It should be possible to identify a variety of olefins which will display the entire range of behavior illustrated in Figure 10 and predicted by eqs 31 and 32.

(6) The equilibrium constant K_1 of the cobalt-carbon bond formation and homolysis reaction of $LCo{-}R_1$

$$LCo + R_1 \rightleftharpoons LCoR_1$$

can be determined in a relatively straight forward manner under conditions employing tertiary-radicals as a radical source.[9] A necessary condition is

$$(k_{-A1} + k_{-B1})[M_1] \gg (k_{-A2} + k_{-B2})[M_2]$$

so that the cobalt complex reacts much more quickly with M_1 rather than M_2. It is only under this condition that the presence of M_2 in the reaction mixture has no influence on the calculation of the apparent K_1. To achieve the range of temperatures required for reliable values of the thermodynamic properties, it is likely that a second monomer derived from another initiator will be present in concentrations which could not be ignored if this condition were not met. For instance, in the measurements for MAN, AIBN could be utilized for part of the temperature range, but other initiators were required for lower temperatures. Because the initiators were chosen to yield radicals which served only as a source of CoH and did not compete effectively for that CoH, they had no influence on the outcome of the measurements. This indicates, however, that care must be taken when utilizing AIBN as the radical source for K_1 measurements for monomers other than MAN. An indication that the initiator-derived monomer is not interfering in the measurements would be that the relative concentration of CoR_2 does not change upon addition of varying concentrations of M_2.

It should be noted that the relative energies of activation for the bond homolysis reactions of CoR_1 and CoR_2 reflect their relative bond strengths. The bond formation reactions are determined only by diffusion control and ought to be very similar. Thus, the reaction is controlled primarily by the relative stabilities of the radicals and the energies of the Co−C bonds formed.

(7) The total number of possible variations of relative rate constants in kinetic Scheme 3 is very large. We have considered only those few variations which we have observed directly. Future investigations may well uncover systems which deviate substantially from the scheme described here utilizing one particular set of simplifying assumptions. For example, we believe that some monomers will undergo monomolecular β-hydrogen elimination (reactions 9 and 10) rather than achieving the same result by homolysis followed by bimolecular abstraction (reactions 7 and 8). It is also very easy to obtain pairs of monomers which both react either rapidly (for instance, methacrylonitrile and methyl methacrylate) or slowly (for instance, cyclopentene and isobutene) with cobalt hydride. Systems with intermediate cases, such as styrene, will be more difficult to interpret and it will be necessary to limit the range of concentrations employed in their investigation, but we believe that all of the systems will be encompassed within the basic set of equations set forth in Scheme 3.

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