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Persistent Radical Effect in Action: Kinetic Studies of Copper-Catalyzed Atom Transfer Radical Addition in the Presence of Free-Radical Diazo Initiators as Reducing Agents

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Kinetic features of the atom transfer radical addition (ATRA) of CCl_4 to 1-octene, styrene, and methyl acrylate catalyzed by $[Cu^{II}(TPMA)Cl][Cl]$ (TPMA = tris(2-pyridylmethyl)amine) in the presence of free-radical diazo initiator (AIBN) as a reducing agent were investigated. For 1-octene, the catalyst concentration was found to affect the alkene conversion and the yield of monoadduct for $[\text{1-octene}]_0/[Cu^{II}]_0$ ratios above 10 000:1. A more pronounced effect of the catalyst loading was observed in the case of methyl acrylate and styrene, due to the formation of AIBN-initiated oligomeric/polymeric side products. For all three alkenes, the optimum reaction conditions were achieved using 5 mol % AIBN relative to alkene. It was also found that excess alkyl halide (CCl_4) was not necessary in ATRA reactions that utilize AIBN as a reducing agent. Kinetic studies of the ATRA process revealed that the rate of alkene consumption was dependent on the concentration and rate of decomposition of the radical initiator, but independent of the concentration of the copper catalyst. However, selectivity of the desired monoadduct ultimately depended on the nature of the catalyst.

Introduction and Background

The origins of atom transfer radical addition (ATRA) can be traced back to 1937 when Kharasch and co-workers discovered the "peroxide effect", which accounted for the anti-Markovnikov addition of HBr to unsymmetrical alkenes in the presence of peroxide initiators.[1] Soon after the discovery of the "peroxide effect", it was recognized that a variety of substrates such as hydrocarbons, polyhalogenated alkanes, alcohols, ethers, amines, aldehydes, ketones, aliphatic acids, and esters and compounds of sulfur, phosphorus, silicon, tin, and germanium can be used in the radical addition to alkenes. In particular, Kharasch et al. investigated the addition of polyhalogenated alkanes (CBr_4, CCl_4, CBr_3Cl, and CCl_3Br) to alkenes in the presence of free-radical initiators or light in a reaction that is today widely referred to as the *Kharasch addition* or *atom transfer radical addition* (Scheme 1).[2,3] Very high yields of the monoadduct were obtained in the case of simple α-olefins (1-hexene, 1-octene, and 1-decene) but were significantly decreased for more reactive monomers such as styrene, methyl acrylate, and methyl methacrylate ($500\ M^{-1}\ s^{-1} < k_p < 10\,000\ M^{-1}\ s^{-1}$). The principal reason for the decreased yield of the monoadduct was radical−radical termination and repeating radical addition to alkene to generate oligomers and polymers. Although radical−radical termination reactions by coupling and disproportionation could be suppressed by decreasing the radical concentration ($R_t \propto [\text{radicals}]^2$), telomerization reactions could not be avoided due to the low chain transfer constant. The research was thus shifted in a direction of finding means to selectively control the product distribution.

In 1956, Minisci et al. attempted thermal polymerization of acrylonitrile in CCl_4 and $CHCl_3$ in a steel autoclave and observed considerable amounts of monoadduct ($CCl_3-CH_2-CHClCN$ with CCl_4 and $CHCl_2-CH_2-CHClCN$ with $CHCl_3$).[4] These results were unexpected because the chain transfer constants of CCl_4 and $CHCl_3$ are not high enough to prevent polymerization of acrylonitrile. In 1961, on the grounds of analogous redox haloalkylations of acrylonitrile, the same authors proposed a mechanism in which iron chlorides (arising from corrosion of the autoclave)

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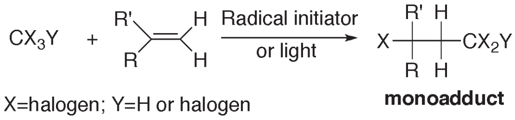
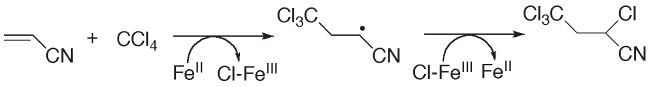
Scheme 1. Kharasch Addition of Polyhalogenated Alkane to Alkene



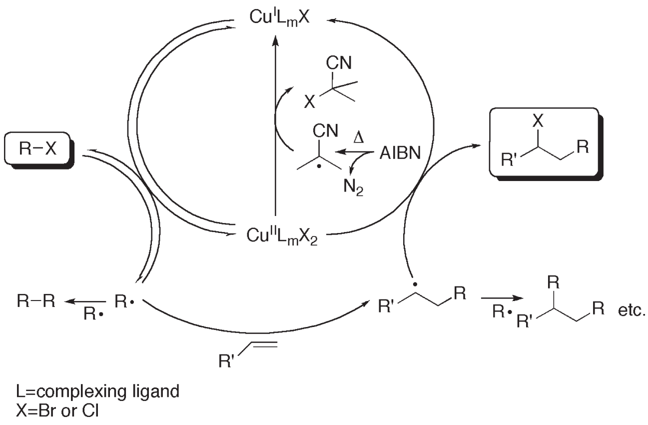
Scheme 2. Iron-Catalyzed ATRA of CCl_4 to Acrylonitrile



played a major role in this process by increasing the chain transfer constant (Scheme 2).[5–10]

This reaction marked the beginning of transition-metal-catalyzed (TMC) ATRA. Since the seminal report by Minisci et al., a number of species were found to be particularly active in the ATRA process, and they included the complexes of Cu, Fe, Ru, and Ni,[11–16] as well as metal oxides[17,18] and zero-valent metals such as Cu(0)[19,20] and Fe(0).[21–23] Great progress has been made in not just controlling the product selectivity but also utilizing a variety of halogenated compounds (alkyl and aryl halides,[9,24,25] *N*-chloroamines,[9] alkylsulfonyl halides,[26–31] and polyhalogenated compounds[26,31–33]), as well as alkenes (styrene, alkyl acrylates, and acrylonitrile). Therefore, TMC ATRA became a broadly applicable synthetic tool.[12–14,34–36]

Scheme 3. Proposed Mechanism for Copper(I) Regeneration in ATRA in the Presence of Free-Radical Diazo Initiator (AIBN) as a Reducing Agent



Until recently, the major drawback of TMC ATRA remained the large amount of catalyst required to achieve high selectivity toward the desired target compound (as high as 30 mol % relative to alkene).[37] This obstacle caused serious problems in product separation and catalyst regeneration, making the process environmentally unfriendly and expensive. The primary reason for the need of a high catalyst concentration was radical termination reactions that led to irreversible accumulation of the persistent radical or deactivator (transition metal complex in the higher oxidation state). Originally, the solution to this problem was found for copper-catalyzed atom transfer radical polymerization (ATRP)[37–41] and was subsequently applied first to ruthenium-[42] and then to copper-catalyzed[43–45] ATRA reactions. In all of these processes, the activator (transition metal complex in the lower oxidation state) is continuously regenerated from the deactivator (transition metal complex in the higher oxidation state) in the presence of reducing agents such as phenols, glucose, ascorbic acid, hydrazine, tin(II) 2-ethylhexanoate, magnesium, and free radical initiators (Scheme 3). Such regeneration compensates for unavoidable radical−radical termination reactions, enabling a significant reduction in the amount of metal catalyst. When applied to the ATRA of CCl_4 to alkenes catalyzed by the $Cp^*Ru^{III}Cl_2(PPh_3)$ complex

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in the presence of 2,2′-azobis(2-methylpropionitrile) (AIBN), turnover numbers (TONs) as high as 44 500 were obtained.[42] Even more impressive TONs were achieved with CBr_4 and the [Cu^{II}(TPMA)Br][Br] (TPMA = tris(2-pyridylmethyl)-amine) complex (as high as 160 000), enabling efficient ATRA reactions in the presence of as little as 5 ppm of copper.[43] Previous TONs for copper-catalyzed ATRA ranged between 0.1 and 10.[14,37] Since the seminal reports by our group[44] and the research group of Severin,[42] this method of catalyst regeneration in ATRA has attracted considerable academic interest[37,45–54] and was even successfully applied to atom transfer radical cyclization (ATRC) and sequential ATRA and ATRC reactions.[52,53,55–57]

While several research groups have utilized this technique for catalyst regeneration in ATRA and ATRC, to the best of our knowledge, the important factors that govern the kinetics of these processes are still not fully understood. This article reports on the kinetic studies of the ATRA of CCl_4 to various alkenes catalyzed by copper(II) complexes in the presence of free-radical diazo initiators as reducing agents.

Experimental Section

General Procedures. All reagents were obtained from commercial sources. Styrene, 1-octene, and methyl acrylate were dried over calcium hydride and degassed prior to use. AIBN was recrystallized from cold methanol and dried at room temperature under a vacuum. Solvents (acetonitrile and toluene) were degassed and deoxygenated using Innovative Technology solvent purifier. Carbon tetrachloride and anisole were deoxygenated by bubbling argon for 30 min before use. Tris(2-pyridylmethyl)amine (TPMA);[58] tris[2-(*N*,*N*-dimethylamino)ethyl]-amine (Me_6TREN);[59] and copper(II) complexes [Cu^{II}(TPMA)-Cl][Cl],[44] [Cu^{II}(Me_6TREN)Cl][Cl],[60] Cu^{II}(PMDETA)Cl_2[61] (PMDETA = *N*,*N*,*N*′,*N*″,*N*″-pentamethyldietheylenetriamine), and [Cu^{II}(bpy)$_2$Cl][Cl][62] (bpy = 2,2′-bipyridine) were synthesized according to published procedures. All other reagents were used as received. Manipulations were performed under argon in a drybox (< 1.0 ppm of O_2 and < 0.5 ppm of H_2O) or using standard Schlenk line techniques. ^{1}H NMR spectra were obtained at room temperature on a Bruker Avance 400 MHz spectrometer with chemical shifts given in parts per million relative to the residual solvent peak ($CDCl_3$, 7.26 ppm). UV−vis spectra were recorded using a Beckman DU-530 spectrometer.

ATRA of CCl_4 to Alkenes. A stock solution containing CCl_4, alkene, and AIBN in the molar ratio 4:1:0.05 ($[\text{alkene}]_0 = 1.4$ M) was prepared in acetonitrile and the internal standard added (anisole for 1-octene and styrene; *p*-methoxybenzene for methyl acrylate). The solution of [Cu^{II}(TPMA)Cl][Cl] in acetonitrile (0.025 M or 5.25×10^{-3} M) was then added in a desired ratio to 1.0 mL of the stock solution in separate vials. The total volume was adjusted by adding acetonitrile to obtain the constant alkene concentration in each reaction mixture ($[\text{alkene}]_0 = 0.95$M). The resulting solutions were then stirred at 60 °C for 24 h under argon. The conversion of the alkene and the yield of monoadduct were determined using ^{1}H NMR spectroscopy. ^{1}H NMR spectra for the products of the addition of CCl_4 to 1-octene, styrene, and methyl acrylate have been published previously.[44] The effect of [CCl4] ($[Cu^{II}]_0/[\text{alkene}]_0/[\text{AIBN}]_0$ = 1:100:5, $[\text{alkene}]_0 = 1.7$ M) and [AIBN] ($[\text{alkene}]_0/[CCl_4]_0/[Cu^{II}]_0$ = 100:400:1, $[\text{alkene}]_0 = 1.0$ M) was investigated following a similar procedure.

Kinetic Studies. The desired amount of [Cu^{II}(TPMA)Cl][Cl], [Cu^{II}(Me_6TREN)Cl][Cl], Cu^{II}(PMDETA)Cl_2, or [Cu^{II}(bpy)Cl]-[Cl] (225 μL, 0.025 M solution in acetonitrile) was added to 2.0 mL of the acetonitrile solution containing CCl_4, alkene, AIBN, and the internal standard ($[CCl_4]_0/[\text{alkene}]_0/[\text{AIBN or V70}]_0$ = 4:1:0.05, $[\text{alkene}]_0 = 1.4$ M) in a 10 mL Schlenk flask equipped with a stirring bar. The alkene concentration in each reaction mixture was maintained at 0.95 M by adding 900 μL of acetonitrile. The reaction flask was then immersed in a 60 °C oil bath. Samples (approximately 100 μL) were taken periodically using purged syringes and analyzed using ^{1}H NMR spectroscopy.

Reduction of Copper(II) Complexes in the Presence of AIBN. Copper(II) solutions were prepared with the following initial concentrations using methanol as the solvent: [Cu^{II}(Me_6-TREN)Cl][Cl]$_0$ = 0.0028 M, [Cu^{II}(TPMA)Cl][Cl]$_0$ = 0.0045 M, [Cu^{II}(PMDETA)Cl_2]$_0$ = 0.0045 M, and [Cu^{II}(bpy)$_2$Cl][Cl]$_0$ = 0.01 M. A catalyst solution (3 mL) and AIBN (10 equiv relative to copper(II) complex) were placed in an air-tight 10 mm quartz cell. The reaction mixture was heated at 60 °C for 3 h and the absorbance at λ_{max} ([Cu^{II}(Me_6TREN)Cl][Cl] = 938 nm, [Cu^{II}-(TPMA)Cl][Cl] = 967 nm, Cu^{II}(PMDETA)Cl_2 = 698 nm, and [Cu^{II}(bpy)$_2$Cl][Cl] = 736 nm) monitored at timed intervals. The concentration of Cu^{II} was determined using extinction coefficient values calculated from Beer−Lambert's law: ε([Cu^{II}(Me_6-TREN)Cl][Cl]) = 413.9 L mol^{-1} cm^{-1}, ε([Cu^{II}(TPMA)Cl][Cl]) = 192.1 L mol^{-1} cm^{-1}, ε(Cu^{II}(PMDETA)Cl_2) = 214.3 L mol^{-1} cm^{-1}, and ε([Cu^{II}(bpy)$_2$Cl][Cl]) = 179.0 L L mol^{-1}cm^{-1}.

Results and Discussion

Effect of [Cu^{II}(TPMA)Cl][Cl] on ATRA of CCl_4 to Alkenes. The effect of catalyst concentration on the alkene conversion and the yield of monoadduct (determined from ^{1}H NMR integration and multiplied by the alkene conversion) in the ATRA of CCl_4 to alkenes was systematically investigated by varying the molar ratio of the catalyst with respect to alkene from 100:1 to 10 000:1, while keeping other reactant concentrations constant. The corresponding plots for the alkene conversion and the percent yield of monoadduct versus catalyst loading are shown in Figure 1. The [Cu^{II}(TPMA)Cl][Cl] complex was quite effective in the ATRA of CCl_4 to 1-octene using as little as 0.02 mol % of the catalyst. A slight decrease in the yield of monoadduct was observed at even lower catalyst loadings (yield = 93%, 7500:1 (0.013 mol %) and yield = 90%, 10 000:1 (0.010 mol %)), which was attributed to incomplete alkene conversions. These results

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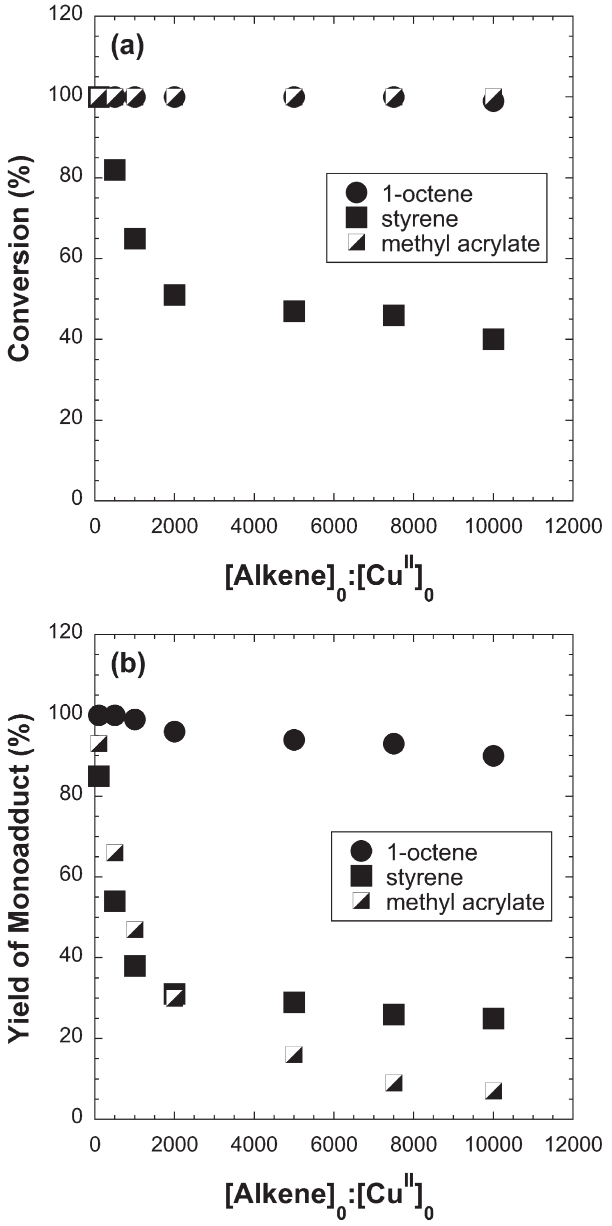

Figure 1. Effect of [Cu^{II}(TPMA)Cl][Cl] on the ATRA of CCl_4 to alkenes. Experimental conditions: time = 24 h, solvent = CH_3CN, T = 60 °C, $[alkene]_0/[CCl_4]_0/[AIBN]_0$ = 1:4:0.05, $[alkene]_0$ = 0.95 M.

clearly indicate that a free-radical diazo initiator (AIBN) provides a constant source of radicals, which continuously reduce [Cu^{II}(TPMA)Cl][Cl] to Cu^{I}(TPMA)Cl. The activator or copper(I) complex is needed to homolytically cleave the CCl_3-Cl bond. A more pronounced effect of the catalyst loading on the alkene conversion and the yield of monoadduct was observed in the case of styrene and methyl acrylate. For styrene, a relatively high yield of the monoadduct was observed at much higher catalyst loadings (alkene-to-catalyst ratio = 100:1). A further increase in the styrene-to-[Cu^{II}(TPMA)Cl][Cl] ratio still resulted in relatively high conversions; however, a more pronounced decrease in the yield of monoadduct was observed. The decrease in the yield of monoadduct was mostly due to the formation of oligomers/polymers, as a result of insufficient trapping of radicals generated from either AIBN (free radical polymerization) or the addition of $CCl_3^\bullet$ to alkene (ATRA) by the copper(II) complex. An even more noticeable effect on the yield of monoadduct was observed in the addition of CCl_4 to methyl acrylate. For this alkene, nearly quantitative conversions were observed regardless of the copper(II) concentrations in the system. However, the percent yield of the monoadduct was found to strongly depend on the alkene-to-catalyst molar ratio. At a 100:1 ratio of methyl acrylate to [Cu^{II}(TPMA)Cl][Cl], the monoadduct was obtained in 93% yield. Furthermore, the yield continuously decreased at lower catalyst loadings and reached a value of only 7% when the ratio of methyl acrylate to copper(II) was 10 000:1.

The results on the effect of [Cu^{II}(TPMA)Cl][Cl] clearly indicate that AIBN is not a very effective reducing agent for alkenes that have high propagation rate constants in free radical polymerization, such as styrene and methyl acrylate. For such alkenes, low-temperature free-radical diazo initiators such as V-70 (2,2′-azobis(4-methoxy-2,4-dimethyl valeronitrile) can be used. In our previous report, this initiator was shown to be a very effective reducing agent, enabling selective formation of the ATRA product with α-olefins and highly active monomers such as methyl acrylate, methyl methacrylate, and vinyl acetate at ambient temperatures using as low as 0.002 mol % of copper.[45] Alternatively, redox-reducing agents that do not generate free radicals, such as magnesium, can also be utilized.[52]

Effect of [CCl_4] on ATRA of CCl_4 to Alkenes. The formation of oligomers/polymers is a common side reaction in ATRA, especially when highly active monomers, such as styrene and methyl acrylate, are used. In the absence of free-radical initiators, oligomers/polymers are formed during ATRA as a result of further monoadduct activation or insufficient trapping of radicals generated in the first addition step by the copper(II) complex (Scheme 3). In order to suppress reactivation of the monoadduct, typically an excess of alkyl halide relative to alkene is used (as high as 4 equiv). The results for the effect of CCl_4 concentration on the ATRA with 1-octene, styrene, and methyl acrylate are summarized in Table 1. Using 1 mol % of [Cu^{II}(TPMA)Cl][Cl], a complete conversion of 1-octene was not observed when the $[1\text{-octene}]_0/[CCl_4]_0$ ratio was 1:1. A further increase in the ratio of CCl_4 to 1-octene allowed for the total consumption of the alkene and quantitative yield of the monoadduct, which remained constant using as high as 6 equiv of CCl_4. Reactivation of the monoadduct is not expected for 1-octene because the resulting C−Cl bond is quite strong.[63] Also, free radical polymerization should not compete with the deactivation processes because α-olefins are known to have very low propagation rate constants.[64]

Complete conversion of styrene and methyl acrylate was also observed in the ATRA using stoichiometric amounts of CCl_4 with 1 mol % of copper catalyst. However, in comparison with 1-octene, the yields of the monoaduct were slighly lower for both alkenes. In addition,

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Table 1. Effect of [CCl_4] on the ATRA of CCl_4 to Alkenes at Various Copper(II) Loadings[a]

	conversion (%)/yield (%)[b]								
	1-octene	styrene			methyl acrylate				
[alkene]$_0$/[CCl_4]$_0$	1 mol % Cu^{II}	1 mol % Cu^{II}	0.2 mol % Cu^{II}	0.02 mol % Cu^{II}	1 mol % Cu^{II}	1 mol % Cu^{IIc}	0.2 mol % Cu^{IIc}	0.1 mol % Cu^{IIc}	0.02 mol % Cu^{IIc}
1:1.0	83/83	100/86	67/40	41/25	100/74	80/71	90/45	95/35	92/22
1:1.5	100/100	100/89	70/48	41/27	100/79				
1:2.0	100/100	100/90	71/46	42/27	100/92	84/72	91/48	94/36	92/21
1:2.5	100/100	100/88	76/48	41/25	100/81				
1:3.0	100/100	100/84	82/53	43/26	100/81	82/69	88/47	94/32	90/20
1:4.0	100/100	100/89	84/55	43/27	100/80	80/68	88/50	95/36	93/21
1:5.0	100/100	100/86	76/50	45/26	100/81	82/71	88/50	92/34	91/20
1:6.0	100/100	100/85	67/46	44/26	100/82	79/67	88/51	92/30	91/19

[a] All reactions were performed in CH_3CN at 60 °C for 24 h with [alkene]$_0$/[AIBN]$_0$ = 1:0.05 and [alkene]$_0$ = 0.95M. [b] The yield is based on the formation of monoadduct and was determined using ^1H NMR spectroscopy (relative errors are ± 10%). [c] Reaction time = 2 h.

Table 2. Effect of [AIBN] on the ATRA of CCl_4 to Alkenes at Various Copper(II) Loadings[a]

	conversion (%)/yield (%)[b]						
	1-octene	styrene			methyl acrylate		
[alkene]$_0$/[AIBN]$_0$	1 mol % Cu^{II}	1 mol % Cu^{II}	0.2 mol % Cu^{II}	0.1 mol % Cu^{II}	1 mol % Cu^{II}	0.2 mol % Cu^{IIc}	0.1 mol % Cu^{IIc}
1:0.01	98/94	82/70	70/37	28/24	100/79	67/40	71/28
1:0.05	100/100	100/89	84/55	45/33	100/80	88/50	95/36
1:0.10	100/99	100/85	90/49	47/35	100/84	93/51	96/35
1:0.15	100/99	100/85	93/47	55/38	100/77	96/52	99/39
1:0.20	100/100	100/85	100/49	65/38	100/79	98/50	100/40

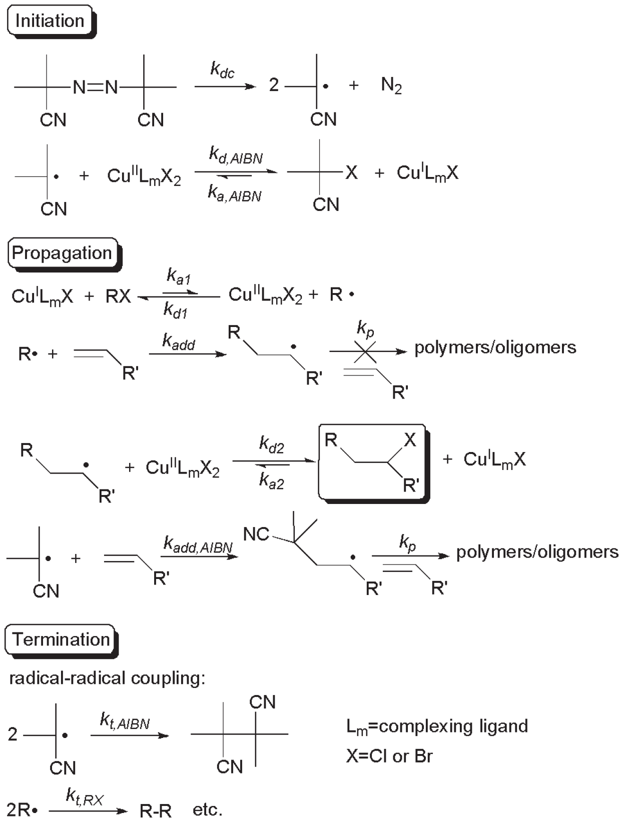
[a] All reactions were performed in CH_3CN at 60 °C for 24 h with [alkene]$_0$/[CCl_4]$_0$ = 1:4 and [alkene]$_0$ = 0.95M. [b] The yield is based on the formation of monoadduct and was determined using ^1H NMR spectroscopy (relative errors are ± 10%). [c] Reaction time = 2 h.

they remained relatively independent of the ratio of alkene to CCl_4. At lower copper(II) catalyst loadings (0.2 and 0.02 mol %, Table 1), a further decrease in the conversion and the yield of monoadduct was observed, but the amount of CCl_4 added did not have a significant effect. These results clearly show that further activation of the monoadduct for methyl acrylate and styrene is much slower than the formation of $CCl_3^\bullet$ radicals generated from the homolytic cleavage of the $CCl_3{-}Cl$ bond. Additionally, the formation of the monoadduct via the cleavage of the $CCl_3{-}Cl$ bond by radicals generated from the decomposition of AIBN only (nonmetal-catalyzed Kharasch addition) is negligible since higher concentrations of CCl_4 in the system have no significant effect on the monoadduct yield. Consistent with our previous studies,[43-45] a decrease in the yield of monoadduct in the ATRA of CCl_4 to methyl acrylate and styrene at lower catalyst loadings (0.2 and 0.02 mol %, Table 1) is induced by free-radical polymerization initiated by AIBN.

Effect of [AIBN] on ATRA of CCl_4 to Alkenes. So far, we have considered the effects of alkyl halide (CCl_4) and [Cu^{II}(TPMA)Cl][Cl] concentrations on the alkene conversion and the yield of monoadduct in ATRA reactions utilizing a free-radical diazo initiator (AIBN) as reducing agent. AIBN is very important component of the reaction mixture because its slow decomposition provides a constant source of radicals that are essential for the regeneration of the activator or Cu^I(TPMA)Cl complex. Table 2 shows the results of the effect of varying AIBN concentrations on the ATRA of CCl_4 to 1-octene, styrene, and methyl acrylate. For all three alkenes, the conversion and the yield of the monoadduct increased as the ratio of AIBN to alkene increased from 0.01:1 to 0.05:1; however, the maximum is achieved at approximately 5 mol % of AIBN (relative to alkene), consistent with our previous observations.[43,44] At high catalyst loadings ([alkene]$_0$/[Cu^{II}]$_0$ = 100:1), a further increase in the AIBN concentration has a small effect on the monomer conversion and the percent yield of monoadduct.

As aforementioned, the major side reaction in copper-catalyzed ATRA in the presence of free-radical diazo initiators as reducing agents is competing radical polymerization. This side reacion is minimized with alkenes that have slow propagation rate constants but is significantly pronounced for alkenes that rapidly polymerize in the presence of radical initiators. The effect of varying free-radical initiator concentration at low catalyst loadings (0.2 and 0.1 mol %) was also investigated for the ATRA of CCl_4 to styrene and methyl acrylate. As evident in Table 2, a significant increase in the percent conversion of the alkene was observed with increasing AIBN concentration. However, the yield of monoadduct remained nearly constant. Since AIBN is a reducing agent in the system, one could speculate that higher AIBN concentrations result in lowering of the overall copper(II) concentration. This in turn decreases the rate of trapping of $CCl_3{-}CH_2{-}CHR'^\bullet$ radicals generated from the addition of $CCl_3^\bullet$ to an alkene (rate $\propto$ [Cu^{II}]), resulting in polymerization/oligomerization. However, this explanation appears to be rather unlikely, because a decrease in the copper(II) concentration will result in a decrease of the monoadduct yield (see Table 1). Therefore, the increase in the conversion for methyl acrylate and styrene is most

Scheme 4. Initiation, Propagation, and Termination Steps in Copper-Catalyzed ATRA in the Presence of Free-Radical Initiator AIBN



likely induced by free radical polymerization initiated by AIBN.

Kinetic Studies. The reaction kinetics for the ATRA process in the presence of free-radical diazo initiators such as AIBN appear to be rather complex. The principal reason is the incorporation of additional reaction steps that involve AIBN. These steps are (a) the decomposition of AIBN to generate free radicals, (b) the reduction of copper(II) to copper(I) in the presence of AIBN, and (c) the free radical polymerization of alkene initiated by AIBN. The elementary reactions for these processes are shown in Scheme 4. The rate of disappearance of alkene (assuming fast trapping of radicals generated in the first addition step ($k_{d2}[\mathrm{Cu^{II}L}_m\mathrm{X}_2] \gg k_p[\text{alkene}]$) and neglecting monoadduct reactivation ($k_{a2} \approx 0$)) is given by the following expression:

$$-\frac{d[\text{alkene}]}{dt} = k_{\text{add}}[\mathrm{R}^\bullet][\text{alkene}] + k_{\text{add, AIBN}}[\mathrm{I}^\bullet][\text{alkene}] + k_{\text{p}}[\mathrm{I-Alk}^\bullet][\text{alkene}]$$

where the first term corresponds to the ATRA process and the second and third ones to free-radical polymerization initiated by AIBN ($\mathrm{I}^\bullet$ denotes radicals formed from the decomposition of AIBN and $\mathrm{I\text{-}Alk}^\bullet$ radicals formed in subsequent additions of $\mathrm{I}^\bullet$ to alkene). In free radical polymerization, the number of molecules reacting in the initiation step is far less than the number in the propagation step for a process producing a high-molecular-weight polymer. To a very close approximation, the former can be neglected, and the polymerization rate is given simply by the rate of propagation.[64] Therefore, the above equation can be simplified to

$$-\frac{d[\text{alkene}]}{dt} = k_{\text{add}}[\mathrm{R}^\bullet][\text{alkene}] + k_{\text{p}}[\mathrm{I}^\bullet][\text{alkene}]$$

If we combine the equilibrium expressions for copper(I) regeneration and activation/deactivation of alkyl halide (RX), the radical concentration ($\mathrm{R}^\bullet$) in the system is equal to

$$\frac{[\mathrm{Cu^IL}_m\mathrm{X}][\mathrm{I-X}]}{[\mathrm{Cu^{II}L}_m\mathrm{X}_2][\mathrm{I}^\bullet]} = \frac{k_{\text{d, AIBN}}}{k_{\text{a, AIBN}}} = \frac{1}{K_{\text{ATRA, AIBN}}}$$

$$\frac{[\mathrm{Cu^{II}L}_m\mathrm{X}_2][\mathrm{R}^\bullet]}{[\mathrm{Cu^IL}_m\mathrm{X}][\mathrm{R-X}]} = \frac{k_{\text{a, 1}}}{k_{\text{d, 1}}} = K_{\text{ATRA, RX}}$$

$$[\mathrm{R}^\bullet] = \frac{K_{\text{ATRA, RX}}}{K_{\text{ATRA, AIBN}}}\frac{[\mathrm{R-X}]}{[\mathrm{I-X}]}[\mathrm{I}^\bullet]$$

Substituting this expression into the original equation for the rate of disappearance of alkene in ATRA yields

$$-\frac{d[\text{alkene}]}{dt} = k_{\text{add}}\frac{K_{\text{ATRA, RX}}}{K_{\text{ATRA, AIBN}}}\frac{[\mathrm{R-X}]}{[\mathrm{I-X}]}[\mathrm{I}^\bullet][\text{alkene}] + k_{\text{p}}[\mathrm{I}^\bullet][\text{alkene}]$$

This equation is not directly usable because it contains a term for the concentration of radicals [$\mathrm{I}^\bullet$] generated from the decomposition of AIBN. However, using steady-state approximation, this concentration can be easily estimated by assuming that the rate of initiation is equal to the rate of termination. In other words,

$$\frac{d[\mathrm{I}^\bullet]}{dt} = 2k_{\text{dc}}[\text{AIBN}] = 2k_{\text{t}}[\mathrm{I}^\bullet]^2 \approx 0$$

$$[\mathrm{I}^\bullet] = \sqrt{\frac{k_{\text{dc}}}{k_{\text{t}}}[\text{AIBN}]}$$

Final substitution of the expression for [$\mathrm{I}^\bullet$] gives the rate of disappearance of alkene in copper-catalyzed ATRA containing a free-radical initiator as a reducing agent (eq 1):

$$-\frac{d[\text{alkene}]}{dt} = \sqrt{\frac{k_{\text{dc}}}{k_{\text{t}}}[\text{AIBN}]}\left(k_{\text{add}}\frac{K_{\text{ATRA, RX}}}{K_{\text{ATRA, AIBN}}}\frac{[\mathrm{R-X}]}{[\mathrm{I-X}]} + k_{\text{p}}\right)[\text{alkene}] \quad (1)$$

From this equation, it is apparent that the rate depends not only on the concentrations of alkene, RX, and I-X, but also on the equilibrium constants $K_{\text{ATRA,RX}}$ and $K_{\text{ATRA,AIBN}}$, addition (k_{add}) and propagation (k_{p}) rate constants for alkene, as well as decomposition (k_{dc}) and termination (k_{t}) rate constants for AIBN. Surprisingly, the rate of alkene consumption is not dependent on the

Table 3. Values of k_{obs} (s^{-1}) for the ATRA of CCl_4 to Alkenes with Varying Concentrations of $[Cu^{II}(TPMA)Cl][Cl]$[a]

$[alkene]_0/[Cu^{II}]_0$	1-octene	styrene	methyl acrylate
100:1	$(2.1 \pm 0.09) \times 10^{-4}$	$(3.8 \pm 0.20) \times 10^{-5}$	$(3.2 \pm 0.28) \times 10^{-4}$
500:1	$(1.7 \pm 0.04) \times 10^{-4}$	$(1.0 \pm 0.14) \times 10^{-5}$	$(4.0 \pm 0.38) \times 10^{-4}$
1000:1	$(1.5 \pm 0.09) \times 10^{-4}$	$(0.7 \pm 0.05) \times 10^{-5}$	$(4.9 \pm 0.15) \times 10^{-4}$

[a] $[alkene]_0/[CCl_4]_0/[AIBN]_0 = 1{:}4{:}0.05$, $[alkene]_0 = 0.95$ M, solvent = CH_3CN, $T = 60$ °C. Errors are given at 95% confidence limits.

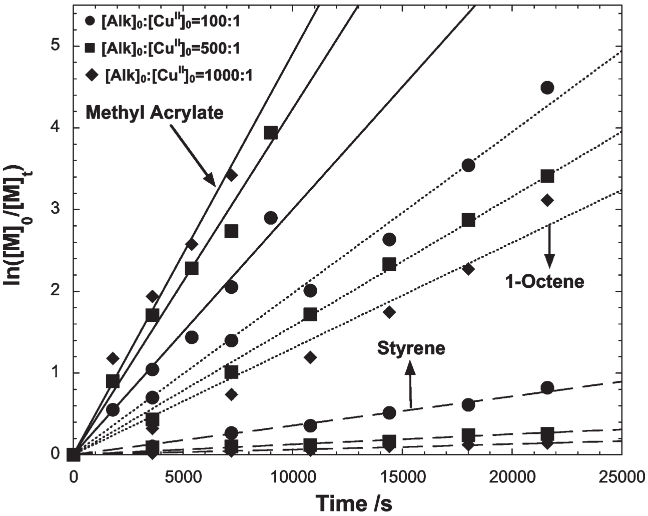


Figure 2. First-order kinetic plots for the ATRA of CCl_4 to methyl acrylate (—), styrene (---), and 1-octene (···) catalyzed by varying $[Cu^{II}(TPMA)Cl][Cl]$ concentrations (1 mol % (●), 0.2 mol % (■), and 0.1 mol % (◆)) in the presence of AIBN. Experimental conditions: $[alkene]_0/[CCl_4]_0/[AIBN]_0 = 1{:}4{:}0.05$, $[alkene]_0 = 0.95$M, solvent = CH_3CN, $T = 60$ °C.

concentrations of copper(I) and copper(II) complexes. This is contrary to the derived rate law for copper-catalyzed ATRA in the absence of a reducing agent (eq 2):[37]

$$-\frac{d[\text{alkene}]}{dt} = \frac{k_{a,1}k_{\text{add}}[\text{Cu}^{\text{I}}\text{L}_m\text{X}][\text{RX}][\text{alkene}]}{k_{d,1}[\text{Cu}^{\text{II}}\text{L}_m\text{X}_2]} = \frac{K_{\text{ATRA}}k_{\text{add}}[\text{Cu}^{\text{I}}\text{L}_m\text{X}][\text{RX}][\text{alkene}]}{[\text{Cu}^{\text{II}}\text{L}_m\text{X}_2]} \quad (2)$$

Several experimental results are consistent with the rate expression for alkene consumption derived in eq 1 and are discussed below.

First-order kinetic plots for the ATRA of CCl_4 to methyl acrylate, styrene, and 1-octene catalyzed by varying $[Cu^{II}(TPMA)Cl][Cl]$ concentrations in the presence of AIBN as a reducing agent are shown in Figure 2. Linear plots were observed for all three alkenes, indicating a constant concentration of radicals. The observed rate constants (k_{obs}) were calculated from the slopes, and the results are summarized in Table 3. The order of the k_{obs} values was as follows: methyl acrylate > 1-octene > styrene. In the case of 1-octene, a 10 times decrease in the concentration of $[Cu^{II}(TPMA)Cl][Cl]$ resulted in only a slight decrease in the observed rate constant ($k_{obs} = (2.1 \pm 0.09) \times 10^{-4}$ s^{-1} (100:1) and $(1.5 \pm 0.09) \times 10^{-4}$ s^{-1} (1000:1)). Similar results were also observed for methyl acrylate ($k_{obs} = (3.2 \pm 0.28) \times 10^{-4}$ s^{-1} (100:1) and $(4.9 \pm 0.15) \times 10^{-4}$ (1000:1)). Relatively small variations in k_{obs} values are consistent with eq 1, which predicts that the rate of alkene consumption should be independent of catalyst concentration. On the other hand, a more pronounced effect of the $[Cu^{II}(TPMA)Cl][Cl]$ concentration was observed for styrene. Increasing the styrene-to-copper(II) ratio from 100:1 to 1000:1 resulted in approximately a 5 times decrease in the observed rate constant ($(3.8 \pm 0.20) \times 10^{-5}$ s^{-1} to $(0.7 \pm 0.05) \times 10^{-5}$ s^{-1}). The origin of this decrease in the rate of styrene consumption is presently not clear. One possibility could include the coordination of styrene radicals to the copper(I) center, which would be more pronounced at higher catalyst loadings. Additionally, the reaction kinetics could be more complicated by the generation of radicals from the thermal decomposition of styrene.[38] We are presently investigating this system by conducting additional experiments along with kinetic modeling.

Table 4. Values of k_{obs} (s^{-1}) for the ATRA of CCl_4 to Styrene and Methyl Acrylate Catalyzed by Different Copper(II) Complexes[a]

Cu^{II} complex	styrene	methyl acrylate
$[Cu^{II}(Me_6TREN)Cl][Cl]$	$(1.24 \pm 0.17) \times 10^{-5}$	$(5.8 \pm 0.11) \times 10^{-4}$
$[Cu^{II}(TPMA)Cl][Cl]$	$(1.28 \pm 0.09) \times 10^{-5}$	$(4.0 \pm 0.38) \times 10^{-4}$
$Cu^{II}(PMDETA)Cl_2$	$(1.26 \pm 0.26) \times 10^{-5}$	$(3.6 \pm 0.36) \times 10^{-4}$
$[Cu^{II}(bpy)_2Cl][Cl]$	$(1.20 \pm 0.23) \times 10^{-5}$	$(3.4 \pm 0.64) \times 10^{-4}$

[a] $[alkene]_0/[Cu^{II}]_0/[CCl_4]_0/[AIBN]_0 = 500{:}1{:}2000{:}25$, $[alkene]_0 = 0.95$ M, solvent = CH_3CN, $T = 60$ °C. Errors are given at 95% confidence limits.

Similar experiments were also conducted with AIBN in order to examine the concentration effect on the reaction rates. For the ATRA of CCl_4 to 1-octene catalyzed by $[Cu^{II}(TPMA)Cl][Cl]$, the apparent reaction order was 0.36 ± 0.09 with respect to AIBN, which is close to 0.5 predicted from the above derived rate law (eq 1). Similarly, the reaction order with respect to AIBN was found to be 0.49 ± 0.08 and 0.31 ± 0.10 in the case of styrene and methyl acrylate, respectively. Furthermore, the rate of consumption of 1-octene, styrene, and methyl acrylate was found to increase as the concentration of alkene or CCl_4 increased. Lastly, consistent with eq 1, the rate decreased as the concentration of I-X (chlorine trapped radicals generated from the decomposition of AIBN, $(CH_3)_2C(CN)Cl$, Scheme 4) increased.

Equation 1 predicts that the rate of alkene consumption in copper-catalyzed ATRA in the presence of a free-radical diazo initiator as a reducing agent should also depend on the ratio of equilibrium constants $K_{ATRA,RX}$ and $K_{ATRA,AIBN}$. In order to examine the effect of the nature of the copper catalyst, several different complexing ligands, namely, TPMA, Me_6TREN, PMDETA, and bpy were utilized in ATRA studies. K_{ATRA} values for copper(I) complexes with these ligands in CH_3CN at

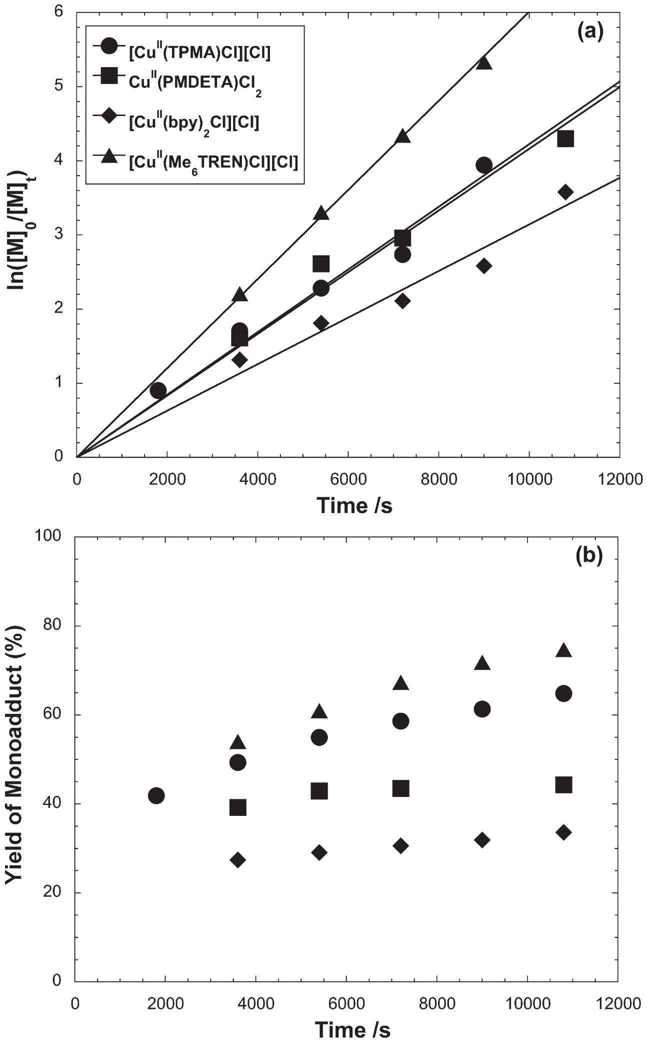


Figure 3. Plots of ln([M]$_0$/[M]$_t$) (a) and percent yield of monoadduct (b) versus time for the ATRA of CCl$_4$ to methyl acrylate catalyzed by copper(II) complexes with TPMA, PMDETA, bpy, and Me$_6$TREN ligands. Experimental conditions: [MA]$_0$/[Cu^{II}]$_0$/[CCl$_4$]$_0$/[AIBN]$_0$ = 500:1:2000:25, [MA]$_0$ = 0.95M, solvent = CH$_3$CN, T = 60 °C.

35 °C have been shown to span more than 4 orders of magnitude (e.g., K_{ATRA} (ethyl 2-bromoisobutyrate) = 1.54×10^{-4} (Me$_6$TREN), 9.65×10^{-6} (TPMA), 7.46×10^{-8} (PMDETA), and 3.93×10^{-9} (bpy)).[65] First-order kinetic plots for the ATRA of CCl$_4$ to methyl acrylate in the presence of different copper(II) catalysts and AIBN are shown in Figure 3a. Linearity was observed for all complexes investigated, indicating constant radical concentration in each reaction system. The observed rate constants (k_{obs}, Table 4) were found not to be very dependent on the nature of the catalyst. For styrene, the value for k_{obs} was approximately 1.2×10^{-5} s^{-1}, and for methyl acrylate, it was found to differ by less than a factor of 2 (3.0−5.0 $\times$ 10^{-4} s^{-1}). Similar results were also obtained from kinetic modeling of mechanistically similar initiators for continuous activator regeneration ATRP.[38] These results indicate that, regardless of the choice of catalyst, the ratio of equilibrium constants $K_{\mathrm{ATRA,RX}}$/$K_{\mathrm{ATRA,AIBN}}$ should remain nearly constant, which is consistent with the rate law derived in eq 1.

Since we have demonstrated that the rate of alkene consumption in copper-catalyzed ATRA in the presence of free-radical diazo initiators is independent of the nature of the catalyst, one question that remains to be answered is whether any copper complex could be used in this catalytic system. In order to answer this question, product selectivity needs to be taken into account. The concentration of deactivator (copper(II) complex) and the deactivation rate constant ($k_{\mathrm{d,2}}$, Scheme 4) play a crucial role. Monoadduct in ATRA will be formed in high yield only if the rate of radical trapping ($k_{\mathrm{d,2}}$[Cu^{II}][R-CH$_2$−CHR′$^{\bullet}$]) is much higher than the rate of radical polymerization (k_{p}[alkene][R-CH$_2$−CHR′$^{\bullet}$]). Since the deactivation rate constant in ATRA is catalyst-dependent[65−67] and the amount of copper(II) in the system is governed by both $k_{\mathrm{d,AIBN}}$ and $k_{\mathrm{a,AIBN}}$, the yield of monoadduct must depend on the nature of the catalyst. As evident from Figure 3b, this was indeed observed. For highly active catalysts such as [Cu^{II}(Me$_6$TREN)Cl][Cl] and [Cu^{II}(TPMA)Cl][Cl], 65−75% yield of the monoadduct was obtained after 3 h. Catalysts with smaller values of K_{ATRA} such as Cu^{II}(PMDETA)Cl$_2$ and [Cu^{II}(bpy)$_2$-Cl][Cl] only yielded 40 and 30% of the monoadduct, respectively.

Under typical experimental conditions (400:1 < [Cu^{II}]$_0$/[CCl$_4$]$_0$ < 10 000:1), we were unable to accurately determine the amount of copper(II) and consequently copper(I) in the ATRA reactions containing AIBN as a reducing agent. The principal reason was that the large amount of CCl$_4$ resulted in the shift of the equilibrium for atom transfer, favoring the copper(II) complex. In order to demonstrate that the amount of copper(II) in the reaction is also governed by both $k_{\mathrm{d,AIBN}}$ and $k_{\mathrm{a,AIBN}}$, UV−vis experiments were performed at 60 °C for a model system containing only the copper(II) complex and AIBN. As shown in Figure 4, gradual conversion of [Cu^{II}(bpy)$_2$Cl][Cl] to [Cu^{I}(bpy)$_2$][Cl] was observed in the presence of AIBN. After 3 h, the original amount of copper(II) complex decreased nearly 85% and remained constant, indicating that the ATRA equilibrium (Cu^{I} + I-X$\Leftrightarrow$X-Cu^{II} + I$^{\bullet}$, I$^{\bullet}$ denotes radicals formed from the decomposition of AIBN, Scheme 4) had been established. The addition of a large excess of CCl$_4$ (200 equiv) to the reaction mixture shifted the equilibrium back to [Cu^{II}(bpy)$_2$Cl][Cl], confirming that the corresponding [Cu^{I}(bpy)$_2$][Cl] was indeed generated in the system. This could also be visually observed in the change of the reaction color from dark red ([Cu^{I}(bpy)$_2$][Cl]) to green ([Cu^{II}(bpy)$_2$Cl][Cl]). The ATRA equilibrium should in theory persist for as long as there is a constant source of radicals in the system generated from the decomposition of AIBN (approximately 5 days for 99% conversion, assuming k_{dc}(AIBN) = 1.0×10^{-5} s^{-1}).[64] After AIBN has been depleted, [Cu^{I}(bpy)$_2$][Cl] will slowly convert to the [Cu^{II}(bpy)$_2$Cl][Cl] complex (as a result of unavoidable radical−radical termination reactions). The kinetics of

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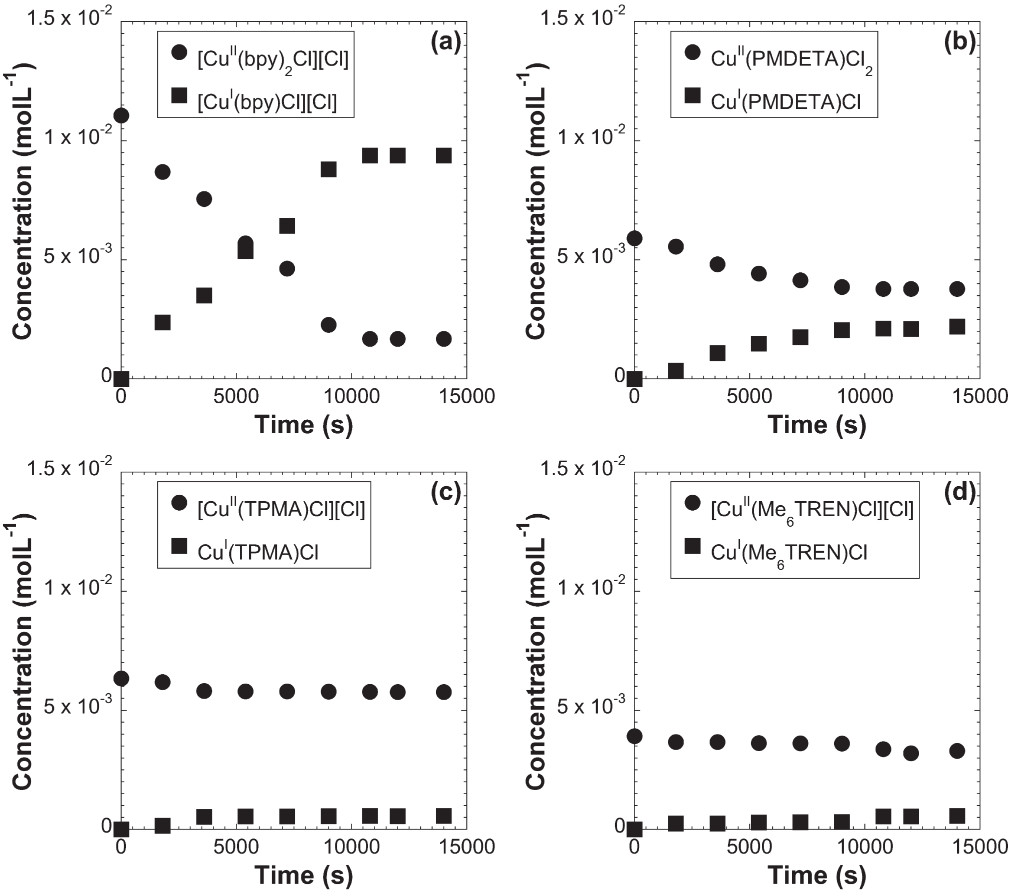

Figure 4. Reduction of copper(II) complexes with bpy (a), PMDETA (b), TPMA (c), and Me_6TREN (d) ligands in the presence of AIBN as a reducing agent in CH_3OH at 60 °C, $[Cu^{II}]_0/[AIBN]_0 = 1{:}10$.

this process are governed by the persistent radical effect,[65] originally developed by Fischer[68−70] and Fukuda.[71]

A decrease in the copper(II) concentration was also observed for complexes with PMDETA, TPMA, and Me_6TREN ligands (Figure 4), although the extent of the change differed significantly. After 3 h, the concentration of $Cu^{II}(PMDETA)Cl_2$ decreased 36%, while only 10% and 15% change was observed for $[Cu^{II}(TPMA)Cl][Cl]$ and $[Cu^{II}(Me_6TREN)Cl][Cl]$ complexes, respectively. These results further confirm that the amounts of copper(II) and copper(I) complexes in ATRA containing AIBN are governed by both $k_{d,AIBN}$ and $k_{a,AIBN}$. Further mechanistic studies of this novel catalytic system are subject to future investigation in our laboratories.

Conclusions

In summary, kinetic features of ATRA of CCl_4 to 1-octene, styrene, and methyl acrylate catalyzed by $[Cu^{II}(TPMA)Cl][Cl]$ in the presence of a free-radical diazo initiator (AIBN) as a reducing agent were investigated. AIBN was a very effective reducing agent for alkenes that have slow propagation rate constants in free radical polymerization such as α-olefins (1-octene), enabling selective formation of the monoadduct using as low as 0.01 mol % of the $[Cu^{II}(TPMA)Cl][Cl]$ complex. For methyl acrylate and styrene, significantly higher catalyst loadings were required in order to minimize free-radical polymerization initiated by AIBN. For all three alkenes, the optimum reaction conditions were achieved using 5 mol % of the free-radical diazo initiator and as little as 1 equiv of CCl_4 relative to alkene. Kinetic studies of the ATRA process revealed that the rate of alkene consumption was dependent on the concentration and rate of decomposition of the free-radical diazo initiator, but independent of the concentration of the copper catalyst. However, the percent yield of the monoadduct ultimately depended on the nature of the catalyst.

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