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Benzoyl-Substituted Ferrocenes: An Attractive New Class of Anionic Photoinitiators

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ABSTRACT: Spectroscopic, photochemical, and photoinitiation studies are reported for a series of monobenzoylferrocenes and 1,1′-dibenzoylferrocenes. These nonionic metallocene complexes absorb strongly in the ultraviolet and visible wavelength regions owing to electronic transitions of mixed ligand field/charge-transfer character. Irradiation of the complexes in methanol results in ring−metal cleavage to yield a benzoyl-substituted cyclopentadienide carbanion and the corresponding half-sandwich iron(II) complex. This process occurs with an appreciable quantum efficiency (>0.30 at 546 nm) for 1,1′-dibenzoylferrocenes; in contrast, monobenzoylferrocenes are appreciably less photosensitive. When the solvent is neat ethyl α-cyanoacrylate, the photogenerated carbanion initiates rapid anionic polymerization of this electrophilic monomer. Several factors that can influence the performance of benzoyl-substituted ferrocenes as anionic photoinitiators are considered.

Introduction

Photoinitiated polymerization reactions form the basis of several commercially important technologies such as the photocuring of coatings, adhesives, and inks, the photopatterning of electronic components, printing plates, and optical waveguides, and the photochemical construction of three-dimensional objects.[1−3] While details of the chemistry will depend on the composition of the system, the general mechanistic features of the photoinitiation process can be represented by a two-step sequence. Initially, the absorption of a photon by the photoinitiator, PI, results in the photochemical generation of one or more reactive species, IN (eq 1). In a subsequent thermal step, IN reacts with a polymerizable substrate to initiate polymer formation (eq 2).

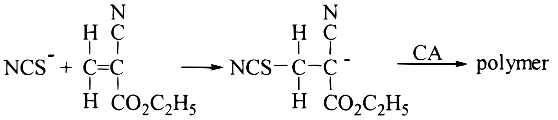
$$\mathrm{PI} \xrightarrow{h\nu} \mathrm{IN} \qquad (1)$$

$$\mathrm{IN} + \text{substrate} \rightarrow \text{polymer} \qquad (2)$$

For the vast majority of photoinitiators, IN is a radical or a strong acid.[4−7] The possibility of initiating useful chemistry with photogenerated anions had received little attention prior to our discovery that solutions of ethyl α-cyanoacrylate (abbreviated CA) containing *trans*-$\mathrm{Cr(NH_3)_2(NCS)_4^-}$ undergo rapid anionic polymerization when irradiated with visible light.[8] We identified the active initiating species in the system as $\mathrm{NCS^-}$ released from a ligand field excited state of the metal complex (eq 3).[9]

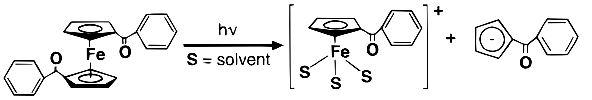
$$trans\text{-}\mathrm{Cr(NH_3)_2(NCS)_4^-} \xrightarrow[\mathrm{CA}]{h\nu} \mathrm{Cr(NH_3)_2(NCS)_3(CA)} + \mathrm{NCS^-} \qquad (3)$$

Addition of this anion to the carbon−carbon double bond of the electrophilic monomer yields a stabilized carbanion (eq 4). Chain-growth polymerization of CA then proceeds from this active anionic site.[10]



$$\mathrm{NCS^-} + \underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}{=}\underset{\mathrm{CO_2C_2H_5}}{\overset{\mathrm{C{\equiv}N}}{\mathrm{C}}} \longrightarrow \mathrm{NCS}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{CO_2C_2H_5}}{\overset{\mathrm{C{\equiv}N}}{\mathrm{C}^-}} \xrightarrow{\mathrm{CA}} \text{polymer} \qquad (4)$$

More recently, we reported that acyl-substituted ferrocenes, particularly benzoylferrocene and 1,1′-dibenzoylferrocene (**II** and **III** in Figure 1), function as photoinitiators for the anionic polymerization of CA.[11] A detailed investigation of the solution photochemistry of **III** revealed that metal−ring bond cleavage occurs in the primary photochemical step to yield a benzoyl-substituted cyclopentadienide, $\mathrm{C_5H_4C(O)C_6H_5^-}$ (eq 5; S is solvent).[12] By analogy to eq 4, we suggested that the addition of this carbanion to CA initiates polymerization.



(5)

We have expanded our investigation of the photoinitiation behavior of benzoyl-substituted ferrocenes to include several analogues of **II** and **III** containing substituents on the phenyl rings (**IV**−**X** in Figure 1). These nonionic sandwich complexes dissolve in a broad range of nonaqueous solvents and absorb strongly in the ultraviolet and visible wavelength regions. They also function as photoinitiators for the anionic polymerization of CA, with the 1,1′-disubstituted ferrocenes generally being superior to their monosubstituted counterparts. Quite interestingly, the presence of electron-withdrawing substituents at the ortho positions of the benzene rings markedly enhances the thermal stability of 1,1′-disubstituted complexes in the monomer solution, thereby lengthening the effective shelf life of the resulting photosensitive formulation. A full account of our results for this promising new series of anionic photoinitiators is reported here.

Experimental Section

Materials. Samples of **I**−**III** were obtained from commercial sources; **I** and **II** were further purified by vacuum

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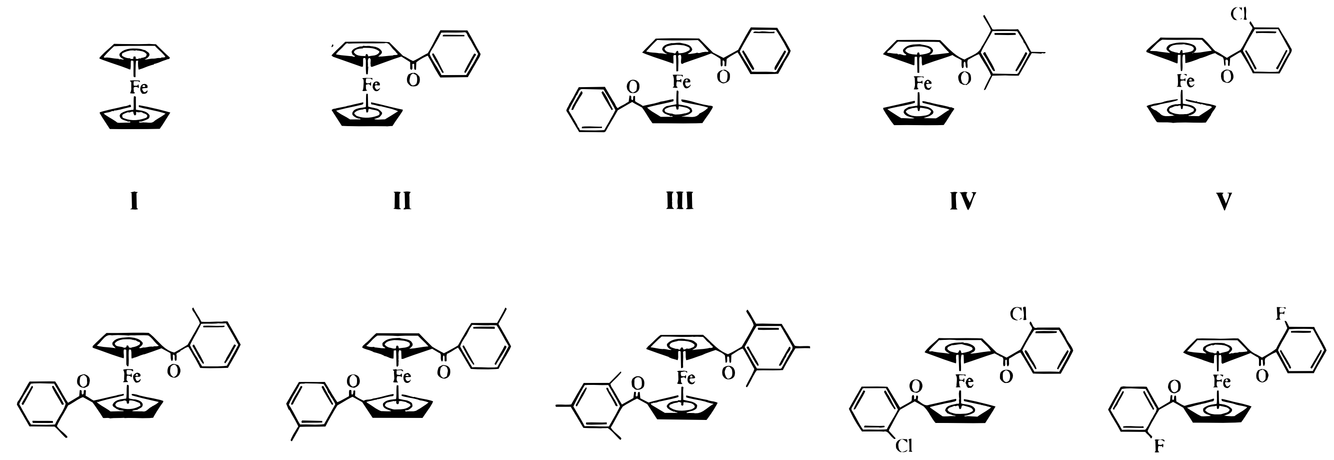

Figure 1. Structures of ferrocenes **I**−**X**.

Table 1. Disappearance Quantum Yield (ϕ_{dis}) Data[a]

1,1′-dibenzoylferrocenes		monobenzoylferrocenes	
complex	ϕ_{dis}	complex	ϕ_{dis}
III	0.45	**II**	0.083
VI	0.41 ± 0.02	**V**	0.098
VII	0.41 ± 0.02		
VIII	0.34 ± 0.00		
IX	0.41 ± 0.01		
X	0.47 ± 0.02		

[a] Experimental conditions: excitation wavelength, 546 nm; light intensity, (1.1 ± 0.1) × 10^{-7} einstein/s; temperature, 22 ± 1 °C; solvent, CH_3OH. Data from ref 12. Where quoted, error limits represent mean deviation of two runs. Estimated accuracy of ϕ_{dis} is 10−15%.

Table 2. Photoinitiation and Thermal Stability Data

run	photoinitiator (PI)	PI concentration		λ_{excit}, nm[a]	t_{photo}, s[b]	t_{therm}, days[c]
		mol/L × 10^3	ppm			
1	**III**	1.06	399	>290	3.8	16
2	**VI**	0.990	398	>290	10	23
3	**VII**	0.995	400	>290	4.3	16
4	**VIII**	0.876	399	>290	37	23
5	**IX**	0.910	401	>290	8.3	86
6	**IX**	0.910	401	>290	10[d]	>64
7	**X**	0.944	387	>290	3.4	52
8	**II**	1.46	404	>290	180	32
9	**IV**	1.26	400	>290	>600	32
10	**V**	1.30	401	>290	340	63
11	**II**	1.90	523	436[e]	>900	*f*
12	**III**	1.61	605	436[e]	38	*f*
13	**III**	2.39	900	546[g]	27	*f*
14	**IX**	2.04	900	546[g]	60	*f*
15	**X**	2.20	900	546[g]	32	*f*
16	none					>180

[a] Excitation wavelength. [b] Irradiation time required for sample to become so viscous that the 8 mm stirring bar ceased to spin. Unless noted otherwise, sample was photolyzed the day of preparation. [c] Time required for a visually noticeable change in the viscosity of a sample stored in the dark at room temperature. [d] Sample was stored in the dark for 64 days prior to irradiation. [e] Light intensity = 7.8 × 10^{-8} einstein/s. [f] Not determined. [g] Light intensity = 1.0 × 10^{-7} einstein/s.

sublimation, while **III** was recrystallized from *n*-hexane. Complexes **IV**−**X** were prepared by standard Friedel−Crafts acylation of **I** with the appropriate acid chloride. Detailed synthetic instructions and characterization data appear elsewhere.[12] Sodium benzoylcyclopentadienide, $Na^+C_5H_4C(O)C_6H_5^-$, was prepared by a published procedure.[13] High-purity CA (99.9% from Loctite Corp.) was used as received; the colorless liquid monomer contained hydroquinone and methanesulfonic acid as scavengers for adventitious radical and basic impurities, respectively. Ethyl α-cyanopropionate (98.2% from TCI America) and spectral grade methanol were used without further purification as solvents in the spectroscopic and photochemical experiments.

Instrumentation. Electronic absorption spectra were recorded at room temperature (21 ± 1 °C) on a Varian DMS spectrophotometer. Continuous photolysis experiments were performed on an Illumination Industries 200 W high-pressure mercury-arc lamp. The 546 nm line was isolated with a narrow-band-pass (10 nm at half-height) interference filter, and light intensity at this wavelength was measured with the Reineckate actinometer.[9] Polychromatic light of wavelengths >290 nm was obtained by passing the full output of the lamp through Pyrex glass.

Photoinitiation and Thermal Stability Studies. Weighed amounts of CA and the ferrocene photoinitiator (Tables 2 and 3) were mixed in high-density polyethylene bottles immediately prior to a photochemical experiment. A 2 mL sample of this solution was placed in a 1 cm rectangular, optically transparent methacrylate plastic cuvette containing an 8 mm magnetic stirring bar. No special precautions were taken to exclude air or ambient moisture. The sample was irradiated at room temperature (typically 23 °C), and t_{photo}, the irradiation time required for it to become sufficiently viscous that the stirring bar ceased to spin, was recorded. For a series of samples run under identical conditions of incident light intensity and stirrer speed, the resulting t_{photo} values provide a simple, yet reliable measure of the relative rates of photoinitiated polymerization.

Thermal stability studies were conducted on samples of CA stored at room temperature in polyethylene bottles wrapped tightly with Parafilm and shielded from light. Periodic visual inspections of sample viscosity were made.

Results and Discussion

Spectroscopy and Solution Photochemistry. Figure 2 compares the electronic absorption spectra of some representative ferrocenes in room-temperature methanol solution. The parent complex (**I**) displays weak bands at 325 and 442 nm that arise from Laporte-forbidden ligand field transitions.[14,15] In contrast, the corresponding bands for the monobenzoylferrocene (**V**) and the 1,1′-dibenzoylferrocene (**III**) occur at longer wavelengths and with significantly higher intensities. These pronounced spectral changes upon adding a benzoyl group to one or both cyclopentadienide rings result from the mixing of charge-transfer character into the ligand field transitions. This charge-transfer contribution can be represented pictorially by a resonance

Table 3. Effect of Scavengers on Photoinitiated Polymerization of CA

photoinitiator (PI)	concn, mol/L × 10^3 (ppm)			
	PI	MSA[a]	HQ[b]	t_{photo}, s[c]
II	2.36 (653)	0.050	9.5	200
II	2.36 (653)	5.1	9.5	>600
II	2.36 (653)	0.050	29	220
III	1.07 (400)	0.050	9.5	3.8
III	1.06 (397)	1.6	9.5	37
III	1.14 (428)	6.0	9.5	>600
III	1.07 (400)	0.050	29	3.6
IX	1.29 (400)	0.050	9.5	6.2
IX	1.30 (403)	1.6	9.5	>600
IX	1.30 (430)	6.0	9.5	>600
IX	1.30 (430)	0.050	29	7.2
X	0.991 (406)	0.050	9.5	3.8
X	0.976 (400)	1.6	9.5	83
X	0.976 (400)	6.0	9.5	>600
X	0.974 (399)	0.050	29	3.4

[a] Methanesulfonic acid (base scavenger). [b] Hydroquinone (radical scavenger). [c] Samples were irradiated with the Pyrex-filtered output of a 200 W high-pressure mercury-arc lamp.

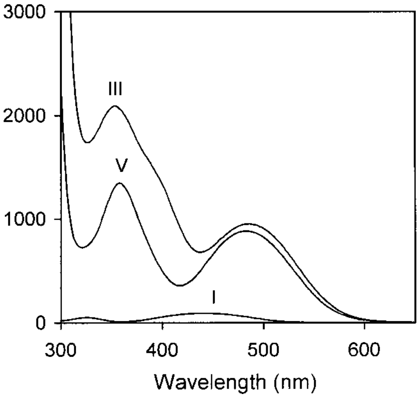

Figure 2. Electronic absorption spectra of ferrocene (**I**), a monobenzoylferrocene (**V**), and a 1,1′-dibenzoylferrocene (**III**) in room-temperature methanol. Additional spectral information about ferrocenes **I**−**X** appears in ref 12.

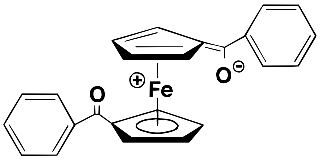

Figure 3. Resonance structure representing the metal-to-ligand charge-transfer character of electronically excited **III**. Formal charges on iron and oxygen atoms are circled.

structure of the type shown for **III** in Figure 3, where the formal charges on iron and oxygen signify a shift of electron density from the metal to the ligand. Conjugation between the π orbitals of the cyclopentadienide ring and the adjacent carbonyl group allows the transferred charge to be spread over several atoms. This charge delocalization stabilizes the resulting excited states and lowers transition energies.[16] Moreover, the mixing of charge-transfer character into the transitions relaxes the Laporte selection rule and increases band intensities.

Placing a benzoyl group on one or both cyclopentadienide rings of ferrrocene also influences photochemical behavior. Thus, while **I** is photoinert in methanol,[17] **II**−**X** readily react in this solvent when irradiated with 546 nm light. A representative example of this photochemistry is shown in Figure 4. Irradiation of an air-saturated methanol solution of **III** causes a steady bleaching of the long-wavelength absorption band of the complex accompanied by an increase of absorbance in the ultraviolet region. The maintenance of an isosbestic point at 372 nm indicates that secondary photolysis of the photoproduct(s) was unimportant during the course of the experiment. Analysis of the photolyte by mass spectrometry reveals that the primary photoreaction is heterolytic ring−metal cleavage to yield the corresponding half-sandwich iron(II) complex and the benzoyl-substituted cyclopentadienide carbanion, $C_5H_4C(O)C_6H_5^-$ (eq 5). Analogous photochemistry occurs for the other ferrocene complexes in the series.

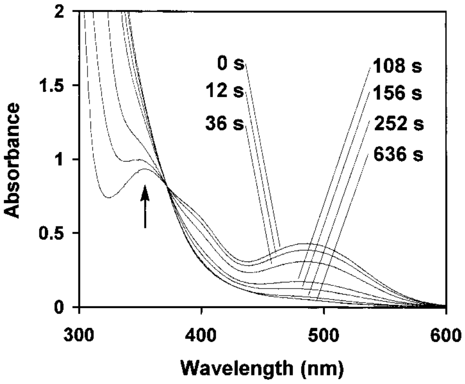

Figure 4. Spectral changes resulting from the 546 nm photolysis of **III** in air-saturated methanol. Light intensity was 1.2 × 10^{-7} einstein/s; irradiation times are noted. Arrow appearing to the left of the isosbestic point indicates that absorbance increases in this region as photolysis proceeds.

Why is ring−metal cleavage an important photochemical process for ferrocenes containing a benzoyl group on one or both cyclopentadienide rings? We can answer this question by considering the bonding changes that occur in these complexes upon populating excited states of mixed ligand field/charge-transfer character. As seen from the resonance structure in Figure 3, these states are characterized by reduced hapticity ($\eta^5 \rightarrow \eta^4$) of a cyclopentadienide ring and enhanced susceptibility of the metal center to nucleophilic attack. The first factor weakens ring−metal bonding, while the second assists the formation of bonds to incoming ligands. Collectively, the two factors facilitate the substitution of a cyclopentadienide ligand by the surrounding solvent. Disappearance quantum yield (ϕ_{dis}) data summarized in Table 1 reveal that 1,1′-dibenzoylferrocenes undergo this process much more efficiently than their monobenzoylferrocene analogues. Thus, the number of benzoyl-substituted rings present in a ferrocene molecule appears to be a key determinant of its excited-state reactivity. In contrast, substituents on the phenyl ring of the benzoyl group exert relatively little influence on the quantum efficiency of ring−metal cleavage. The electron-withdrawing fluorine atoms in **X** increase ϕ_{dis} relative to the electron-releasing methyl groups in **VI**, but the effect is not large. Steric effects may be responsible for the slightly diminished photosensitivity of **VIII**, since only this complex contains two ortho substituents on each phenyl ring for shielding the metal from nucleophilic attack by solvent.

Photoinitiated Polymerization Studies. Ferrocenes **II**−**X** dissolve readily in neat CA to yield solutions that show no visual change in viscosity for at least 2 weeks when stored in the dark at room temperature. Upon exposure to light, however, these solutions polymerize to an increasingly viscous syrup, which then solidifies.[18] As described in the Experimental Section, we determined the relative rates of this photoinitiated process by measuring t_{photo}, the irradiation time required for the solution to become so viscous that a magnetic stirring bar in the sample cell ceased to spin. Data compiled in Table 2 reveal that polymerization occurs much more rapidly for samples containing 1,1′-dibenzoylferrocenes (runs 1−7) than for those containing monobenzoylferrocenes (runs 8−10). While these results were obtained with polychromatic (>290 nm) excitation, similar behavior is observed for absorbance-matched samples of **II** (run 11) and **III** (run 12) irradiated at 436 nm. The latter finding establishes that the disparity in photoinitiator performance between the two classes of complexes is not an artifact of the stronger absorption of short-wavelength light by 1,1′-dibenzoylferrocenes (Figure 2). Within the 1,1′ series, rapid polymerization occurs even when irradiating with low-energy green light (runs 13−15). Hence, these complexes allow wide latitude in the selection of excitation source.

Valuable information concerning the nature of the primary initiating species (IN in eqs 1 and 2) was obtained from measurements of t_{photo} in the presence of scavengers. As seen in Table 3, increasing the concentration of hydroquinone, a known radical scavenger, does not affect t_{photo} for any of the ferrocene complexes examined. Similarly, t_{photo} for **II** and **III** is independent of the oxygen content of the sample. In contrast, increasing the concentration of the strong proton donor, methanesulfonic acid, causes t_{photo} to rise dramatically for all of the complexes. We infer from these observations that IN is not a radical, but instead is a Bronsted base that initiates the anionic polymerization of CA. Protons inhibit this polymerization process by scavenging the initiating species and/or the reactive anionic sites on growing polymer chains.

We considered the possibility that IN is the CA radical anion formed via transfer of an electron from the photoexcited benzoyl-substituted ferrocene to a neighboring monomer molecule (shown for **III** in eq 6; an asterisk denotes an electronically excited species). Precedent for this type of process is provided by **I**, which, in an electron-accepting medium such as CCl_4, forms a photoactive ground-state complex with the solvent that is characterized by a charge-transfer-to-solvent (CTTS) absorption band at ~310 nm. Irradiation of this ground-state complex in the wavelength region of the CTTS band causes the one-electron oxidation of **I** to the ferricenium cation and reduction of solvent to its radical anion.[19−21] However, we find no evidence for a CTTS band in the electronic absorption spectrum of CA solutions of **III**, nor do we observe spectral changes consistent with the formation of a ferricenium cation when **III** is irradiated at 546 nm in ethyl α-cyanopropionate, a nonvinylic analogue of CA that cannot undergo polymerization.[22] Consequently, excited-state electron transfer (eq 6) can be discounted as the pathway responsible for generating the active initiating species.

$$\mathbf{III} \xrightarrow{h\nu} \mathbf{III}^* \xrightarrow{\text{CA}} \mathbf{III}^+ + \text{CA}^{\bullet -} \qquad (6)$$

Since the photolyses of **II**−**X** release benzoyl-substituted cyclopentadienide ions (e.g., eq 5), we investigated the alternative possibility that these carbanions, which should be strong Bronsted bases, play the role of IN. The sodium salt of a representative example, $C_5H_4C(O)C_6H_5^-$, was independently synthesized and its reactivity toward CA tested. Addition of one drop of a 1.3×10^{-3} M acetonitrile solution of the carbanion to ~1 mL of the monomer causes rapid (1−2 s) solidification accompanied by the evolution of heat. This vigorous response demonstrates that cyclopentadienide ions of the type generated photochemically from **II**−**X** can serve as effective initiators for the polymerization of CA.

Further evidence for assigning these carbanions as the primary initiating species comes from a comparison of ϕ_{dis} (Table 1) and t_{photo} (Table 2) values. Ferrocene complexes characterized by a high quantum efficiency of carbanion formation ($\phi_{dis} > 0.3$) invariably give the shortest polymerization times. This correlation strongly suggests that 1,1′-dibenzoylferrocenes are more effective photoinitiators than monobenzoylferrocenes because they undergo more efficient photochemical release of the species, namely, benzoyl-substituted cyclopentadienide ions, responsible for initiating CA polymerization.

Another factor (besides ϕ_{dis}) that can influence photoinitiator performance is the reactivity of the initiating species toward the substrate (i.e., eq 2). Within the 1,1′-dibenzoylferrocene series, ϕ_{dis} (Table 1) and t_{photo} (Table 2) values fall within narrow ranges for **III**, **VI**, **VII**, **IX**, and **X**. This behavior indicates that the carbanions photochemically released from these complexes exhibit very similar reactivities toward CA. The one exception is **VIII**, for which t_{photo} seems unduly low in relation to ϕ_{dis}.

Thermal Stability of Photoinitiator/Monomer Solutions. Data compiled in Table 2 reveal some interesting trends in the thermal stabilities of various CA samples. Values of t_{therm}, the time required for a sample stored in the dark to undergo a visually noticeable increase in viscosity, are uniformly lower for solutions containing **II**−**X** than for the pure monomer. At first glance, this observation suggests that the ferrocene photoinitiators accelerate the thermal polymerization of CA. While these complexes undoubtedly are involved, we suspected that an equally important role is played by the methanesulfonic acid present in the commercial monomer as a scavenger for basic impurities. This strong acid should be capable of protonating the carbonyl oxygen atoms in **II**−**X**.[23] Subsequent reaction(s) of the protonated species could result in (1) formation of an active thermal initiator and/or (2) complete consumption of the acid scavenger with resulting initiation by adventitious base. Accordingly, we reasoned that lengthening the effective shelf life of photoinitiator/monomer solutions would require stabilizing benzoyl-substituted ferrocenes against attack by acid. One strategy toward this end involves sterically hindering access to the carbonyl site by placing ortho substituents on the phenyl ring. As seen from the results for **III** (run 1) and **VI** (run 2), adding a single ortho methyl group increases t_{therm} by ~50%, but no further stabilization occurs from placing methyl groups at both ortho positions as in **VIII** (run 4). Thus, steric considerations alone cannot explain the thermal stability data in Table 2. Equally, if not more, important is the electronic effect of the substituent as evidenced by the marked lengthening of t_{therm} caused by electron-withdrawing groups such as Cl in **IX** (run 5) and F in **X** (run 7). The inductive effect of these groups should render the carbonyl oxygen less susceptible to protonation and thus retard photoinitiator degradation. While additional studies are needed to provide a more complete mechanistic picture of thermal polymerization in CA solutions containing **II−X**, our results establish that placing electron-withdrawing ortho substituents on the phenyl rings of the benzoyl-substituted complexes produces a salutary effect on solution shelf life.

Finally, Table 2 compares the photosensitivities of two identically prepared solutions of CA containing **IX** (runs 5 and 6). One solution was irradiated immediately after preparation, while the other was stored in the dark at room temperature for 64 days prior to photolysis. The nearly identical values of t_{photo} demonstrate that long-term storage did not adversely affect photoinitiator performance.

Concluding Remarks

The 1,1′-dibenzoylferrocenes, **III** and **VI−X**, comprise an attractive new class of anionic photoinitiators. Irradiation of these complexes in neat ethyl α-cyanoacrylate monomer liberates a cyclopentadienide carbanion that initiates rapid polymerization. While substituents on the phenyl ring of the benzoyl group have little effect on the quantum efficiency of carbanion release, they can dramatically alter the thermal stability of photoinitiator/monomer solutions. We have exploited this behavior to design photopolymerizable formulations that possess high light sensitivity and long shelf life (see runs 5 and 7 in Table 2). Our continuing studies of these photoinitiators, and the search for other monomers that can undergo photoinitiated anionic polymerization, will be the subjects of future reports.

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