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Photodissociation of Diphenylchloromethane: Ion-Pair Formation in the Presence of Ferrocene

John D. Simon and Kevin S. Peters*†

Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138

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The photolysis of diphenylchloromethane in the presence of ferrocene has been examined by using picosecond absorption spectroscopy. Within 35 ps following photolysis, ferricenium and the diphenylmethyl radical are observed. These species in turn decay with the same rate. The electrochemical data on these intermediates support the assignment of the decay process to the oxidation of the diphenylmethyl radical by ferricenium yielding ground-state ferrocene and the diphenylmethyl cation, chloride anion ion pair.

Introduction

The dynamics of ion pairs in nonaqueous solutions has been the subject of several recent experimental studies.[1] Ion pairs are frequently invoked as reaction intermediates,[2] and an understanding of the solvent dynamics associated with ion-pair formation and separation is essential for the development of a complete picture of organic reaction mechanisms. In order to examine the solvent reorganization associated with the dissociation of a leaving group characteristic of nucleophilic displacement reactions, i.e., Cl^-, we decided to examine the dynamics and solvent dependence on the photolysis of diphenylchloromethane.

It was anticipated that photolysis would result in the formation of the corresponding contact ion pair.[3] The ensuing solvation could then be monitored by examining the time dependence on the shape of the absorption spectrum of the diphenylmethyl cation. However, photolysis in even polar solvents (acetonitrile, Me_2SO) resulted in the formation of a radical pair; no evidence for the formation of ions was detected.[4]

In order to bypass this problem and generate Cl^- as the leaving group in this system, we examined the photochemistry of diphenylchloromethane in the presence of ferrocene. Ferrocene, as well as other metallocenes, are well-known for their ability to photoreduce chlorinated compounds.[5] Photolysis of ferrocene in neat carbon tetrachloride (excitation of the $FeCp_2 \rightarrow RX$ charge-transfer complex) results in the formation of ferricenium, Cl^-, and the $CCl_3\cdot$ radical.[5a] In the presence of diphenylchloromethane, a similar reaction would be expected.

Experimental Section

The picosecond (ps) absorption spectrometer has previously been described in detail.[6] Briefly, a Quantel YG-400 is used to generate 30-ps pulses at 1.06 and 355 nm. The 355-nm light is used for excitation. Transient absorption spectra are recorded by using a picosecond continuum generated by focusing the fundamental into a solution of carbon tetrachloride and chloroform (500–800 nm). The continuum light is dispersed by a Jarrel Ash (JY-200) monochrometer and imaged onto a vidicon array (PAR 1215-1216-1254) detection system. Transient absorption spectra were recorded at 35, 310, and 860 ps and 1.3, 2.1, 4.5, 9.3, and 19.0 ns by using fiber optics. This technique ensures that the overlap between the excitation and probe beams remains fixed as the time delay is changed.

Ferrocene (Aldrich) was recrystallized from ethanol. Diphenylchloromethane was purified by vacuum distillation and stored under argon. Spectrograde acetonitrile (Aldrich), spectrograde cyclohexane (Kodak), and dimethyl sulfoxide (Mallinckrodt) were stored over 4A molecular sieves for at least 48 h prior to use. Ethanol (U. S. Industrial Chemicals Co.) was used without purification. Samples were degassed by nitrogen purging.

Table I. Rate of Decay of the Diphenylmethyl Radical

solvent	ϵ	$10^{-8}k_{\text{obsd}}$, s^{-1}
cyclohexane	2	1.15
ethanol	25	1.25
acetonitrile	37	1.94
dimethylsulphoxide	57	3.56

Results

In order to detect the existence of a ground-state complex between diphenylchloromethane and ferrocene, we examined the ground-state UV–vis absorption spectrum of ferrocene in the presence of varying amounts of diphenylchloromethane. The data indicate an increase in absorption in the region between 300 and 400 nm similar to that observed in the presence of chloroform and carbon tetrachloride,[5] supporting the formation of a ground-state complex between the two species.

Photolysis of the ground-state diphenylchloromethane (0.1 M)–ferrocene (0.02 M) complex in cyclohexane at 355 nm results in formation of the ferricenium cation (λ_{max} = 617 nm[5a]) and the diphenylmethyl radical (λ_{max} = 530 nm[7]) within 35 ps (Figure 1). Between 35 ps and 20 ns following photolysis, we observed a decay in the intensity of the absorption spectra of both species. Both ferricenium and the diphenylmethyl radical decay with the same rate. Photolysis in acetonitrile, Me_2SO, and ethanol results in

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[†] Camille and Henry Dreyfus Teach Scholar and Alfred P. Sloan Fellow.

(1) (a) Simon, J. D.; Peters, K. S. *J. Am. Chem. Soc.* **1982**, *104*, 6542. (b) Simon, J. D.; Peters, K. S. *J. Phys. Chem.*, in press.

(2) (a) Ashby, E. C.; Goel, A. B.; DePriest, R. N.; Prasad, E. S. *J. Am. Chem. Soc.* **1981**, *103*, 973. (b) Olah, G. A.; Krishnamurthy, V. V. *Ibid.* **1982**, *104*, 3987. (c) Ashby, E. C.; Goel, A. B. *Ibid.* **1981**, *103*, 4983. (d) Liotta, D.; Sainsane, M.; Waykole, L. *Ibid.* **1983**, *105*, 2922. (e) Ashby, E. C.; Goel, A. B.; DePriest, R. N. *Ibid.* **1981**, *103*, 5623.

(3) Dissociation to ion pair is observed in the trityl chloride system. Manring, L.; Peters, K. S., to be submitted for publication in *J. Am. Chem. Soc.*

(4) (a) Hilinski, E. F.; Rentzepis, P. M. *Acc. Chem. Res.* **1983**, *16*, 224. (b) Huppert, D.; Rand, S. D.; Reynolds, A. H.; Rentzepis, P. M. *J. Chem. Phys.* **1982**, *77*, 1214.

(5) (a) Traverso, O.; Scandola, F. *Inorg. Chim. Acta* **1970**, *4*, 493. (b) Traverso, O.; Sostero, S.; Mazzocchin, G. *Ibid.* **1974**, *11*, 237. (c) Bozak, R. E. *Adv. Photochem.* **1972**, *8*, 227.

(6) Simon, J. D.; Peters, K. S. *J. Am. Chem. Soc.* **1983**, *105*, 4875.

(7) For an excitation spectrum see: Izumida, T.; Tname, Y.; Ichikawa, T.; Yoshida, H. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 235. The absorption band is similar to that observed in the case of the ketyl radical of benzophenone. If we assume that the two radicals have similar extinction coefficients, ϵ = 3000 L mol^{-1} cm^{-1} (Schaeffer, C. G.; Peters, K. S. *J. Am. Chem. Soc.* **1980**, *102*, 7566), we would expect to see ~6:1 ratio in absorption intensity for diphenylmethyl radical:ferricenium. This is consistent with the observed intensities (Figure 1).

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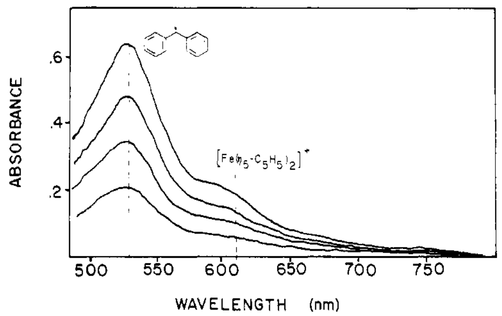


Figure 1. Transient absorption spectra for the photolysis of 0.02 M ferrocene–0.1 M diphenylmethylchloromethane in cyclohexane: A, top, 310 ps following excitation; B, 2.1 ns following excitation; C, 4.5 ns following excitation; D, bottom, 9.3 ns following excitation.

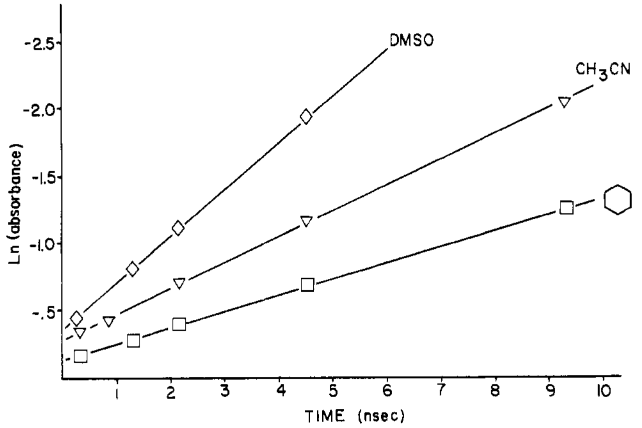
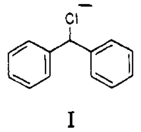


Figure 2. Rate plot for the decay of the diphenylmethyl radical. Solvents: dimethyl sulfoxide (Me_2SO), acetonitrile, and cyclohexane.

similar behavior but different decay rates (Table I and Figure 2).

Discussion

The current mechanism for the photoreduction of chlorocompounds by metallocenes involves the excitation of a ground-state donor–acceptor complex. Excitation results in electron transfer from ferrocene to the chloro compound, resulting in the formation of ferricenium, Cl^- and the resulting hydrocarbon radical.[4a] Our experiments with diphenylchloromethane support this general scheme. However, the time resolution of our experiment allows us to examine this reaction in much greater detail. Excitation of the charge-transfer band results in the transfer of an electron from ferrocene to diphenylchloromethane. In order to ascertain if carbon–chlorine bond cleavage is concomitant with the transfer of the electron, the relative intensity of the absorption spectrum of ferricenium and the diphenylmethyl radical between 30 and 150 ps following photolysis were examined. If the species I has a



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finite lifetime (>50 ps), we would expect to see a faster rise in the concentration of ferricenium with a slower increase in the concentration of radical. However, for all solvents examined, the maximum absorption intensity for both ferricenium and diphenylmethyl radical is observed immediately following photolysis. The absorption intensities observed are consistent with the conclusion that ferricenium is formed concomitant with the appearance of the radical;[7] thus the lifetime of this species must be less than 20 ps due to rapid carbon–chlorine bond cleavage.

Once dissociated, we see no change in the line shape of the diphenylmethyl radical between 35 and 300 ps following photolysis. As a result, we are unable to examine the dynamics of the ensuing radical, ion solvation that is occurring as the chloride ion diffuses into solution.[8] However, between 300 ps and 20 ns following photolysis, we observe simultaneous decays of the diphenylmethyl radical and ferricenium.

As the diphenylmethyl radical and ferricenium decay with the same kinetics, only three possible mechanisms can explain the observed data. First, there could be a bimolecular reaction occurring between the two species to form the cyclopentadienyl addition product. A second possibility involves the oxidation of chloride ion by ferricenium, resulting in a formation of ferrocene, and fast recombination of the diphenylmethyl and chlorine radicals. A third possibility is that the diphenylmethyl radical is being oxidized to the diphenylmethyl cation by ferricenium. If the latter occurs, we will form the desired ion pair between the diphenylmethyl cation and chloride ion, allowing for the examination of the ion-pair recombination dynamics.

Radical addition to cyclopentadienyl rings has previously been observed for the photolysis of ferrocene in carbon tetrachloride.[9] However, in our sample, no net chemistry is observed.[10] Furthermore, we would expect the resulting addition product to have a visible absorption spectrum; however, no new transients were detected. These arguments would seem to rule out the possibility of a bimolecular reaction between the two species.

The reduction potential of the diphenylmethyl cation has been determined to be −0.4 to −0.5 V (vs. SCE).[11] The reduction potential for the ferrocene/ferricenium couple has been measured to be +0.35 V (vs. SCE).[12] Thus the electrochemical data supports the conclusion that ferricenium is capable of oxidizing the radical. The reduction potential of $Cl\cdot$ is approximately +3.8 V (vs. SCE),[13] indicating that ferricenium cannot oxidize the Cl^- anion. On the basis of the above arguments, we conclude that the decay of ferricenium and the diphenylmethyl radical results from radical oxidation by ferricenium. This conclusion is supported by other known examples of radical oxidation by ferricenium.[14]

Examination of the rate of radical decay in the various solvents examined shows a correlation with solvent polarity. For the solvents studied, the rate of radical oxidation increases with increasing dielectric constant. With respect to the aprotic solvents studied, the observed rate of oxidation is consistent with previous studies of ion-pair stability in these solvents.[1,8] As the solvent polarity decreases, the amount of contact ion-pair formation between ferricenium and the chloride anion should increase. Significant ion pairing between ferricenium and the chloride anion should reduce the strength of ferricenium as an

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[8] (a) Simon, J. D.; Peters, K. S. *J. Am. Chem. Soc.* **1982**, *104*, 6152. (b) References 1 and 5.

[9] Geoffroy, G. L.; Wrighton, M. S. "Organometallic Photochemistry"; Academic Press: New York, 1979; pp 242–248.

[10] No change in the UV-vis absorption spectrum is observed after repeated photolysis of the sample solutions.

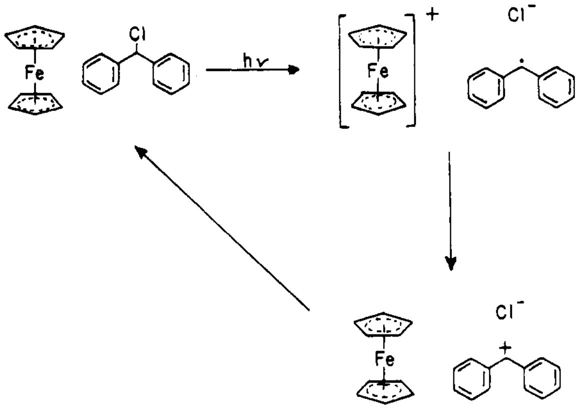
[11] Plesch, P. H.; Sestakoa, I. *J. Chem. Soc. B* 1971, 1337.

[12] (a) Holloway, J. D. L.; Geiger, W. E. *J. Am. Chem. Soc.* **1979**, *101*, 2038. (b) Kuwana, T.; Bublitz, D. E.; Hoh, G. *Ibid.* **1960**, *82*, 5811.

[13] The reduction potential for Cl_2^- is +1.09 V (vs. SCE). The bond strength of Cl_2 is 2.52 eV. Thus, the reduction potential for the $Cl^+/Cl\cdot$ couple is ~3.6 eV. Data from: "Handbook of Chemistry and Physics"; Weast, R. C., Ed.; CRC Press: Cleveland, OH, 1975.

[14] Teitelbaum, Z.; Meyerstein, D. *Proc. Int. Conf. Coord. Chem., 16th* 1974, R56.

Scheme I



oxidant. Thus, the slowest rate of radical oxidation being observed in cyclohexane is consistent with the preponderance of contact ion pairs in this solvent. In ethanol, hydrogen bonding effects must be considered. We have previously found that ethanol is superior to acetonitrile in supporting solvent separated ion pairs,[1] and, on the basis of this observation, we would have expected to observe a faster rate of radical oxidation in ethanol. It is possible that the observed decrease in rate in changing the solvent from acetonitrile to ethanol is due to hydrogen bonding effects on the oxidation potential diphenylmethyl radical.

Summary

The mechanism for the reaction of ferrocene and diphenylmethylchloride is given in Scheme I. Electron transfer from a ground-state complex results in rapid carbon-chlorine bond cleavage relative to electron transfer, forming ferricenium, Cl^-, and the diphenylmethyl radical. The radical is then oxidized by ferricenium forming ferrocene and the diphenylmethyl cation, chloride anion ion pair. Work is currently underway to examine the ensuing ion-pair dynamics as well as other ion-pair-induced reactions using metallocenes as catalysts.

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Registry No. $FeCp_2$, 102-54-5; diphenylmethyl cation chloride anion, 87263-01-2; ferricenium, 12125-80-3; diphenylmethyl radical, 4471-17-4; diphenylchloromethane, 90-99-3.

Cobalt Carbonyl Cluster Radicals in Irradiated $HCo(CO)_4$/Kr Mixtures[†]

S. A. Fairhurst, J. R. Morton, and K. F. Preston*

Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R9

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The EPR spectra of two binuclear cobalt carbonyl cluster radicals have been detected at 77 K in γ- and UV-irradiated solid solutions of $HCo(CO)_4$ in Kr. Partial analyses of the powder spectra suggest assignments to a hydrogen-bridged dimer, $HCo_2(CO)_8$, of C_{2v} symmetry for one species and to a nonbridged anion, $Co_2(CO)_8^-$, of D_{3d} or D_{2d} symmetry for the other.

Introduction

A natural extension of our spectroscopic studies of mononuclear metal carbonyl radicals[1-4] is the investigation of polynuclear species, i.e., metal carbonyl cluster radicals. With one notable exception,[5] however, our attempts to incorporate such species into single-crystal hosts have been unsuccessful. We have therefore resorted to the examination of irradiated polycrystalline samples in the hope of generating and characterizing paramagnetic metal carbonyl clusters. Research in this particular area is already being pursued in several laboratories.[6-8] Unfortunately, in many instances the spectral line widths of species detected in organic or metal carbonyl hosts are large and assignments are accordingly uncertain. In our experience, krypton is a superlative host[9] for the examination of powder EPR spectra. It is totally inert, a surprisingly good solvent, and is stable toward ionizing radiation and exhibits narrow-line EPR spectra in many cases. Moreover, small molecules become mobile in krypton above 90 K, suggesting a method of generating cluster species. In the case of irradiated solutions of $HCo(CO)_4$ in Kr this possibility has been realized: the initial free radical products of irradiation disappear on annealing and are replaced by binuclear cobalt carbonyl radicals. The EPR spectra and structure of these species are described in this article.

Experimental Section

Hydridocobalt tetracarbonyl, $HCo(CO)_4$, was synthesized[10] by the acidification of the complex formed from dicobalt octacarbonyl and dry pyridine. ^{13}C-enriched $HCo(CO)_4$ was produced from the complex which had been exchanged with 99% ^{13}C-enriched CO,

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[†] NRCC No. 22738.

(1) Lionel, T.; Morton, J. R.; Preston, K. F. *J. Chem. Phys.* **1982**, *76*, 234.

(2) Fairhurst, S. A.; Morton, J. R.; Preston, K. F. *J. Chem. Phys.* **1982**, *77*, 5872.

(3) Lionel, T.; Morton, J. R.; Preston, K. F. *J. Magn. Reson.* **1982**, *49*, 225.

(4) Boyer, M. P.; Le Page, Y.; Morton, J. R.; Preston, K. F.; Vuolle, M. J. *Can. J. Spectrosc.* **1981**, *26*, 181.

(5) Lionel, T.; Morton, J. R.; Preston, K. F. *Inorg. Chem.* **1983**, *22*, 145.

(6) Peake, B. M.; Robinson, B. H.; Simpson, J.; Watson, D. J. *Inorg. Chem.* **1977**, *16*, 405.

(7) Krusic, P. J.; San Filippo, J., Jr.; Hutchinson, B.; Hance, R. L.; Daniels, L. M. *J. Am. Chem. Soc.* **1981**, *103*, 2129.

(8) Hayashida, S.; Kawamura, T.; Yonezawa, T. *Inorg. Chem.* **1982**, *21*, 2235.

(9) Boate, A. R.; Morton, J. R.; Preston, K. F. *Chem. Phys. Lett.* **1978**, *54*, 579.

(10) Sternberg, H. W.; Wender, I.; Friedel, R. A.; Orchin, M. *J. Am. Chem. Soc.* **1953**, *75*, 2717.

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