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# Electron Transfer of Carbonylmetalate Radical Pairs: Femtosecond Visible Spectroscopy of Optically Excited Ion Pairs

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## Abstract

Charge transfer excitation at 640 nm of the cobaltocenium tetracarbonylcobaltate ion pair,  $[\text{Cp}_2\text{Co}^+ | \text{Co}(\text{CO})_4^-]$ , was monitored in 1,2-dichloroethane solution by femtosecond transient visible absorption spectroscopy. The absorption prepares a neutral radical pair that can undergo spontaneous back electron transfer, and which shows a double peaked spectrum with features at 760 and 815 nm at 3 ps delay time. Transient decay times of  $5.8 \pm 0.5$  ps were measured by monitoring the decay of  $\text{Co}(\text{CO})_4$  at 757 nm and 780 nm, and these are assigned to the back electron transfer step. The ET kinetics are consistent with the previously reported rates of electron transfer that were measured for specific vibrational states by picosecond transient IR.

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## Introduction

In low to medium dielectric constant solvents the ion pair,  $[\text{Cp}_2\text{Co}^+ | \text{Co}(\text{CO})_4]$ , has been shown to have a weak charge transfer band in the visible spectrum.[1] Optical excitation of this band directly creates a neutral radical pair, and this radical pair can spontaneously electron transfer (ET) to form the initial ion pair or react with solvent or other molecules to form photochemical products. The charge transfer character of the visible absorption in the ion pair has been extensively studied, and radical spectra with microsecond resolution have been measured to confirm the radical separation in some solvents [1]. In very low dielectric constant solvents the ET step is much faster than the radical separation, and this step can be directly studied by spectroscopy.

The rate of electron transfer (ET) in this ion pair has been studied in one of our laboratories by picosecond pumping at 600 nm and IR probing of the CO stretching mode with 2-3 ps pulses [2,3]. This work reported the vibrational state dependent electron transfer rates for the radical pair,  $[\text{Cp}_2\text{Co} | \text{Co}(\text{CO})_4]$ , in 1,2 - dichloroethane solution [3] for quantum numbers  $v = 0$  and  $v = 1$  in the CO stretching mode of the  $\text{Co}(\text{CO})_4$  species. The ET decay times (inverse rate) of the  $v=1$  level was  $8 \pm 1$  ps and the  $v=0$  level was  $17 \pm 1$  ps, with a small long component of 400 ps for  $v=0$ . The fast decays are from direct ET to reform the ion pair, and the long component is assigned to a small amount of diffusional separation in the neutral pair leading to delayed ET. The results obtained with transient IR spectroscopy provide great detail, but there is a need to prove that the observed rates are from a major species. For example, the major channel for ET may have been unresolved with 2-3 ps pulses, in which case the IR experiments would have been monitoring a subset of the species that had slower ET. Therefore, we undertook a transient visible absorption experiment with ~100 femtosecond resolution in order to confirm the time scale for spontaneous electron transfer.

Visible spectroscopy has been used to monitor charge transfer transients following 10 ns laser excitation of  $[\text{Cp}_2\text{Co}^+ | \text{Co}(\text{CO})_4]$ . These experiments were done in acetone [1], and a transient species that absorbs with a peak at 790-800

nm was identified as the 17 electron radical  $\text{Co}(\text{CO})_4$ . The spontaneous back electron transfer to regenerate the ion pair has a time constant of 10  $\mu\text{s}$  [1].

## Experiments

The femtosecond transient visible spectroscopy apparatus was previously described [4]. The apparatus uses single wavelength detection of a broadband continuum through a monochromator at 1 kHz excitation rate, and the optical time delay of the pump beam is used to measure kinetic traces at 100 fs/point. For this experiment the pump beam at 640 nm was 1.6  $\mu\text{J}$  in energy and 150 fs in duration. A visible continuum pulse was used for a probe beam and the pump and probe beam were arranged at the magic angle to remove orientational effects. The compound was synthesized following the procedures described previously [1]. The solvent 1,2 - dichloroethane (99+%, Aldrich) was dried by storing over 4 Å molecular sieves and deoxygenated with dry nitrogen before use. The sample was prepared under nitrogen in a glovebox, and typical sample concentration gave an absorbance of one at 640 nm for a 1 cm path in a stirred, sealed cell.

## Results

Figure 1 shows a transient visible spectrum at 3 ps after the charge transfer excitation with a 150 fs pulse at 640 nm, and this spectrum is assigned to the  $\text{Co}(\text{CO})_4$  radical from prior work [1]. The low value of excitation energy and very small visible extinction coefficient of about  $150 \text{ M}^{-1}\text{cm}^{-1}$  at 640 nm only allowed formation of small concentrations of transient species. Significant signal averaging was required to obtain spectra, where one point was obtained every 1 nm. The data of Figure 1 is displayed with a line obtained by simple 7 point polynomial smoothing for alternate points (about 15 nm). Resolved features cannot be assigned in this spectrum without additional experiments to remove the noise, but there appears to be two major peaks centered at 760 and 815 nm. Extension of the wavelength range to about 1000 nm is needed to examine hot band features. The spectral extinction of the charge transfer band in this region is

significantly smaller than the transient species, and the optical bleaching of the charge transfer band is a negligible component.

Figure 2 shows the time dependence of transient absorbance at 757 nm for the  $\text{Co}(\text{CO})_4$  radical created by CT absorption at 640 nm. With our 150 fs time resolution, the rise time is instrument limited, as is expected for charge transfer absorption directly leading to radical formation. The data was fit with a single exponential, and a decay time constant of  $5.8 \pm 0.5$  ps was extracted from the fitting, where the 95% confidence level is 0.5 ps. Inadequate signal-to-noise is available to probe for heterogeneity of decays, especially for longer components, and a single exponential is sufficient for these data.

## Discussion

Our result in 1,2-dichloroethane solution indicates that the time constant of back electron transfer is  $5.8 \pm 0.5$  ps. This result is consistent with the transient IR spectroscopic results in the same solvent, and is much faster than the reported 10  $\mu\text{s}$  in acetone.[1]

The earlier transient IR experiments [2,3] pumped the charge transfer band at 600 nm, and this work showed that ET is faster than vibrational relaxation for the high frequency CO stretching vibration at  $2000 \text{ cm}^{-1}$ . The vibrational relaxation of this mode is probably longer than the 40 ps measured for the ion pair [5], and may be as long as the  $148 \pm 26$  ps measured [6] for the CO stretch mode of neutral  $\text{Co}(\text{CO})_3\text{NO}$ . The IR experiments and the visible kinetics reported here are not easily compared without more experiments. Multiple component decays in the visible transient will only be seen if the monitor wavelength at 757 nm is measuring several vibrational states simultaneously. One other wavelength at 780 nm was also checked and had similar decays, although there is more noise due to less absorbance. The unknown vibrational assignment of the radical spectrum is likely to be more important than the differences in Franck-Condon factors between the 640 nm excitation of these experiments and the 600 nm excitation of the IR experiments.

The spectra reported by Bockman and Kochi [1] in acetone show a single peak at about 780-790 nm. In Figure 1 we show a spectrum centered in the same region, but with a small dip at 780 nm. Both spectral scans went to about 850 nm, but a greater range is desired in future work to examine hot band features. The microsecond spectra are for vibrationally relaxed radicals, while the spectrum of Figure 1 is for vibrationally excited radicals in a neutral pair. As discussed above, the vibrational excitation of the  $2000\text{ cm}^{-1}$  mode remains in the radical for very long times. An interesting question is whether the low frequency modes decay in  $\leq 2$  ps, as was assumed by the IR experiments. If we suppose that some low frequency mode, such as a totally symmetric ligand-metal mode might be vibrationally relaxing on the 5-6 ps time scale, we would then identify the kinetic trace of Figure 2 at 757 nm with decay from both vibrational relaxation and ET. This hypothetical interpretation can be studied in future work (see next paragraph), but it is sufficient to note that the  $5.8 \pm 0.5$  ps decay at 757 nm is consistent with ET decay times *at least* as long as 5.8 ps. The similar decay at 780 nm, which is the maximum absorption of the vibrationally cold spectrum, suggests that low frequency modes may not be important in this spectral region. From other studies of low frequency vibrations [7], we expect such features to be most prominent at the long wavelength edge of the absorption. Consequently, we assign only ET kinetics to the 5.8 ps decay.

The spectrum of Figure 1 can be repeated with greater pump intensity and/or more signal averaging, and we expect that the known vibrational excitation of the CO stretch will be involved in the Franck-Condon factors for the spectrum, and therefore give new features at longer wavelengths. Therefore, in future work a series of kinetic decays throughout the transient spectrum should show heterogeneity, and these decays can be cross correlated with the IR studies of ET to assign vibrational regions in the spectrum, even if the bands are not spectrally resolved. In addition, direct measure of fast vibrational relaxation for low frequency modes may be separable from ET rates in the longer wavelength region of the spectrum.

The prior visible spectroscopy of the  $\text{Co}(\text{CO})_4$  radical showed a lifetime of 10  $\mu\text{s}$  in acetone [1], which is reasonable for diffusive re-encounter and ET. If the spontaneous ET in the initially formed radical pair is not fast enough to compete efficiently with diffusion, then there will be a significant yield of free radicals. The ET in acetone is likely to be significantly slower than in dichloroethane because the energy gap between the neutral pair and the ion pair is increased in the more polar solvent. Times for diffusional separation in a low viscosity solvent like acetone may be 200-300 ps, and if ET decays are 100-300 ps, then ET would only partially compete with diffusion. For example, in a 10 ns pulsed experiment, the kinetics of a 200 ps ET rate would be unresolved, but diffusion would create a large yield of free radicals.

### Conclusion

Charge transfer excitation at 640 nm of the cobaltocenium tetracarbonylcobaltate ion pair,  $[\text{Cp}_2\text{Co}^+ | \text{Co}(\text{CO})_4^-]$ , was monitored in 1,2-dichloroethane solution by femtosecond transient visible absorption spectroscopy. The absorption prepares a neutral radical pair that can undergo spontaneous back electron transfer (ET), and which shows a double peaked spectrum with features at 760 and 815 nm at 3 ps delay time. Transient decay times of  $5.8 \pm 0.5$  ps were measured by monitoring the decay of  $\text{Co}(\text{CO})_4$  at 757 nm and 780 nm, and these are assigned to the back electron transfer step. The ET kinetics are consistent with the previously reported rates of electron transfer that were measured for specific vibrational states by picosecond transient IR. Kinetic traces throughout the broad visible spectrum of the radical are needed for more complete comparisons with both ET kinetics measured by transient IR and vibrationally relaxed visible spectra reported on long time scales in more polar solvent.



## Acknowledgment

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## References

1. Bockman, T. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1989**, *111*, 4669.
2. Spears, K. G.; Arrivo, S. M.; Wen, X. *SPIE Proceedings*, **1994**, v2138, (in press).
3. Spears, K. G.; Wen, X.; Arrivo, S. M.; *J. Phys. Chem.* (to be published, 9/29/94).
4. Wiederrecht, G.P; Watanabe, S.; Wasielewski, M.R. *Chem. Phys.* **1993**, *176*, 601.
5. Wen, X. and Spears, K. G., to be published.
6. Angel, S.A.; Hansen, P.A., Heilweil, E.J.; Stephenson, J.C. *Ultrafast Phenomena VII*, ed. Harris, C.B., Ippen, E.P, Mourou, G.A. and Zewail, A.H., Springer-Verlag, Berlin, 1990, p480.
7. Elsaesser, T.; Kaiser, W. *Annu. Rev. Phys. Chem.* **1991**, *v42*, 83.

## Figure Captions

**Figure 1.** Spectrum of  $[\text{Cp}_2\text{Co}^+ | \text{Co}(\text{CO})_4]$  in 1,2 dichloroethane solution at 3 ps after excitation by a 640 nm, 150 fs pulse. Probe wavelength is at 1 nm intervals, and the solid curve is a smoothed spectrum obtained with a 7 point polynomial. The absorption is assigned to the  $\text{Co}(\text{CO})_4$  radical species.

**Figure 2.** Transient decay of absorbance at 757 nm with 150 fs resolution. The rise is instrument limited, and the decay is fit with a single exponential of  $5.8 \pm 0.5$  ps.

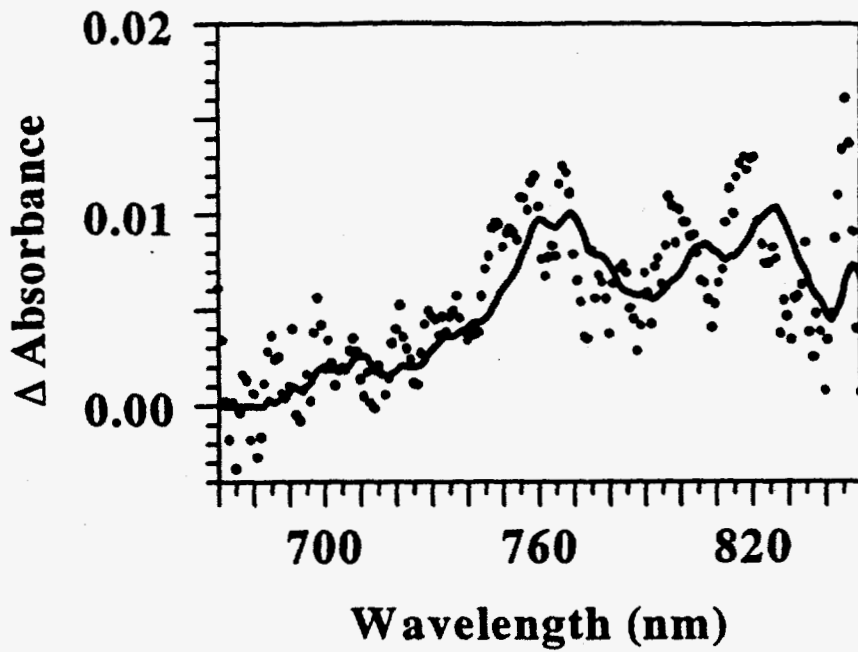


FIG 1

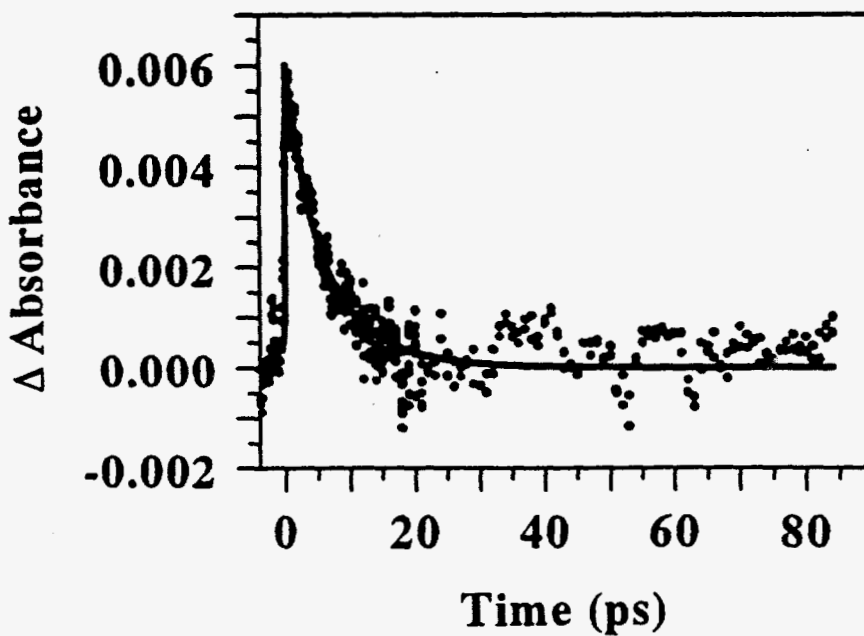


FIG 2