

Observation of a Salt Effect in the Chain Disproportionation Reaction of $\text{Cp}_2\text{Fe}_2(\text{CO})_4$ with dppe (1,2-Bis(diphenylphosphino)ethane)

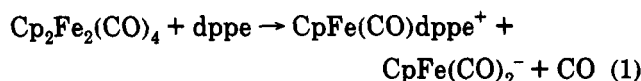
Michael P. Castellani, E. Todd Hesse, and David R. Tyler*

Department of Chemistry, University of Oregon, Eugene, Oregon 97403

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Summary: The chain disproportionation reaction of $\text{Cp}_2\text{Fe}_2(\text{CO})_4$ with dppe (1,2-bis(diphenylphosphino)ethane) exhibits a normal salt effect in the presence of $[\text{NBu}_4^+][\text{PF}_6^-]$. This fact was established by showing that the rate constant for the reaction increased linearly with the concentration of $[\text{NBu}_4^+][\text{PF}_6^-]$. The normal salt effect explains the curvature in the pseudo-first-order plots of $\log([\text{Cp}_2\text{Fe}_2(\text{CO})_4]_t - [\text{Cp}_2\text{Fe}_2(\text{CO})_4]_\infty)$ vs time in those reactions without added salt: the buildup of ionic products induces a salt effect which increases the rate.

Several years ago, we reported a kinetics study of the chain disproportionation reaction of $\text{Cp}_2\text{Fe}_2(\text{CO})_4$ with dppe (1,2-bis(diphenylphosphino)ethane) (eq 1).¹ The



purpose of the study was to distinguish among three reasonable chain mechanisms that had been proposed for the reaction. A mechanistic distinction was possible because the rate law for the reaction was $3/2$ -order (rate = $k[\text{dppe}]^{1/2}[\text{Cp}_2\text{Fe}_2(\text{CO})_4]$), a result consistent with only one of the pathways (Scheme 1).¹ (Reaction 1 is reversible;² therefore, the $\text{CpFe}(\text{CO})_2^-$ product is captured by reacting it with the CH_2Cl_2 solvent (eq 5). The net reaction in CH_2Cl_2 is given by eq 6.)

A curious feature of the kinetics study was that pseudo-first-order plots of $\log([\text{Cp}_2\text{Fe}_2(\text{CO})_4]_t - [\text{Cp}_2\text{Fe}_2(\text{CO})_4]_\infty)$ vs time were linear for 4-5 half-lives, but they showed slight curvature in the direction of a larger rate constant at longer reaction times (Figure 1). In the original report,¹ no explanation was offered for the curvature. However, to complete the mechanistic study and to make sure an important mechanistic point was not overlooked, we have since investigated the origin of the curvature. This note reports the results of our study.

Results and Discussion

The curvature in Figure 1 is reminiscent of that seen in the kinetics plots of organic $\text{S}_\text{N}2$ reactions in which two neutral species react to form ionic products.³ (These are type II reactions in the Ingold classification.⁴) In the absence of added electrolytes, the ionic strength of the medium increases in these reactions, and the rate constant

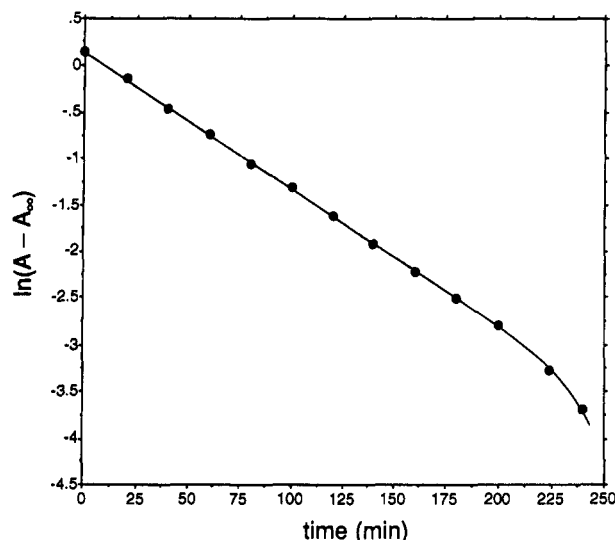
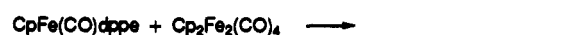


Figure 1. Pseudo-first-order plot for the reaction of $\text{Cp}_2\text{Fe}_2(\text{CO})_4$ with dppe ($[\text{dppe}] = 0.10 \text{ M}$, $[\text{Cp}_2\text{Fe}_2(\text{CO})_4] = 2.2 \times 10^{-3} \text{ M}$; 23°C ; CH_2Cl_2). No $[\text{NBu}_4^+][\text{PF}_6^-]$ or other salt was added to the reaction solution.

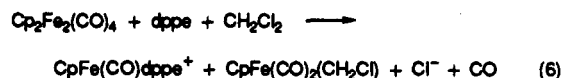
Scheme 1. Chain Disproportionation Mechanism for the Reaction of $\text{Cp}_2\text{Fe}_2(\text{CO})_4$ with dppe



17e



overall:



increases because of a "normal salt effect".^{5,6} An extension of these results to eq 6 suggests that the curvature in Figure 1 is likewise induced by a salt effect caused by an increase in the ionic strength of the solution as the reaction progresses. To test this hypothesis, reaction 6 was run in CH_2Cl_2 solutions containing varying amounts of $[\text{NBu}_4^+][\text{PF}_6^-]$. This salt is an inert electrolyte in this system, and reaction 6 occurred as written. The dependence of the rate constant for reaction 6 on the salt concentration is

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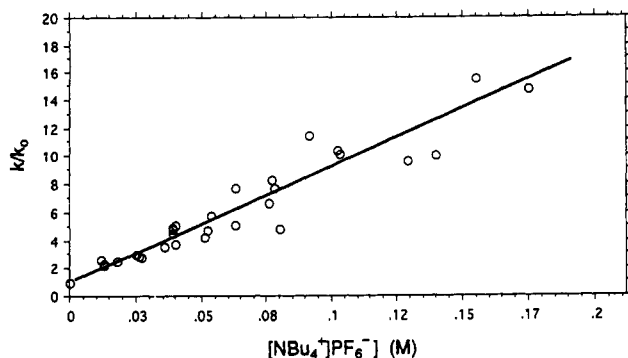


Figure 2. Plot of k vs the concentration of $[\text{NBu}_4^+][\text{PF}_6^-]$ (23°C ; CH_2Cl_2).

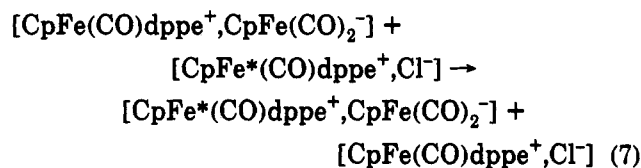
shown in Figure 2. Note the linear increase in the rate constant as the salt concentration increases; i.e., the reaction displays a normal salt effect.^{6,7} As expected, the $\log([\text{Cp}_2\text{Fe}_2(\text{CO})_4]_t - [\text{Cp}_2\text{Fe}_2(\text{CO})_4]_\infty)$ vs time plots for reactions run in the presence of salt did not show any curvature at long reaction times because the ionic strength of these systems is effectively constant throughout the reaction.

A normal salt effect is typical for a reaction of two neutral species that forms ionic products.^{4,5} For example, rate constants for various Menshutkin reactions (the reactions of tertiary amines with alkyl halides to form quaternary salts) increase in the presence of added inert salts.^{8,9} The normal salt effect is generally attributed to the stabilization of a developing charge-separated transition state by dipolar interactions with the ions.⁴⁻⁶ In the case of reaction 1, the rate-determining step in the chain reaction is the electron transfer between the 19-electron species and a dimer molecule (eq 4).¹ It is suggested that stabilization of this transition state by the ionic medium leads to the observed increase in the rate constant. (In ideal solutions, the theoretical relationship between the rate constant and the concentration of the salt is a logarithmic one. However, in practice, a linear dependence is usually observed.¹⁰ Also note that Bunton and Robinson have shown that manipulation of the reactants' energy can also be important in causing the normal salt effect.¹¹)

As mentioned in the introduction, reaction 1 is reversible, as are many metal-metal bond disproportionation reactions.¹² It is for this reason that CH_2Cl_2 is used as the solvent, because it efficiently captures $\text{CpFe}(\text{CO})_2^-$ and

thus prevents it from back-reacting.^{1,2} It was previously demonstrated that another method for inhibiting the back-reaction is to increase the polarity of the solvent.¹² Thus, an alternative, but unlikely, explanation for the origin of the curvature in Figure 1 is that CH_2Cl_2 does not completely capture the $\text{CpFe}(\text{CO})_2^-$ and the larger rate constants in the presence of salt are due to an inhibition of the disproportionation back-reaction. In terms of the net reaction in eq 6, this alternative explanation would argue that reaction 1 is reversible but that the reverse reaction rate constant decreases as the ionic strength of the medium increases. A slower back-reaction would allow CH_2Cl_2 to compete more effectively for $\text{CpFe}(\text{CO})_2^-$ (eq 5), and the net forward rate (of eq 6) would increase correspondingly. This explanation is untenable, however, because as discussed previously,² capture of $\text{CpFe}(\text{CO})_2^-$ by CH_2Cl_2 is quantitative.

Finally, the curvature in Figure 1 cannot be attributed to a "special salt effect".^{5,6,13} The reason is straightforward: exchange of the product ions with the initial ion pair formed in the electron transfer would result in no net change (eq 7).



In summary, the curvature in the pseudo-first-order kinetics plots for reaction 6 is likely attributable to an increase in the ionic strength of the solution as the reaction progresses. The phenomenon is completely explainable in terms of the proposed chain mechanism for the reaction (Scheme 1), and no modification of the mechanism is necessary to account for the observation. Finally, this phenomenon is quite general: similar "self-catalysis" effects have been observed in other bimolecular reactions of two neutral species which form ions.^{3,4,14}

Experimental Section

All manipulations of air-sensitive materials were carried out under a nitrogen atmosphere by using standard Schlenk or vacuum-line techniques. When appropriate, solids and solutions were handled under a nitrogen atmosphere in a Vacuum Atmospheres glovebox. Materials were purified and reactions carried out as previously described,¹ except that $[\text{NBu}_4^+][\text{PF}_6^-]$ was added to the reaction mixture before addition of the solvent. $[\text{NBu}_4^+][\text{PF}_6^-]$ (Fluka) was recrystallized from CH_2Cl_2 /pentane.

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(7) Ingold⁴ separated the effect of added salts into "ionic strength" effects and "specific" salt effects. The former effects are attributed to the stabilizing or destabilizing effects caused by the "ionic atmosphere" surrounding the reactants and transition state. Specific salt effects are attributed to properties of the ions other than their net charge (e.g., their size, shape, charge distribution, and polarizability).

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(9) Decreases in the rate constants have also been observed.⁸ These decreases are attributable to specific interactions of the salts with the reactants.

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(14) $\text{S}_{\text{N}}1$ -type reactions typically show this behavior as well.³⁻⁶