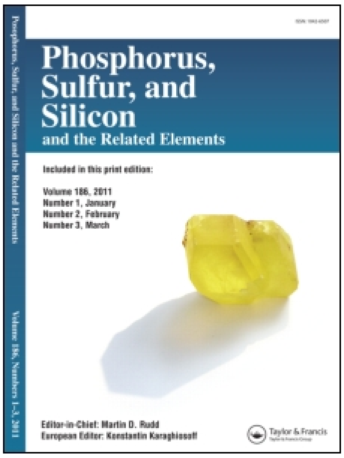

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The Magic Salt Effects of Sodium Hexafluorophosphate

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THE MAGIC SALT EFFECTS OF SODIUM HEXAFLUOROPHOSPHATE

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Dedicated to Professor Alan H. Cowley,
our Distinguished Friend and
a Master in the Chemistry of Main Group Elements
on the occasion of his 60th Birthday

The $Na^+PF_6^-$ salt changes the course of reactions between neutral or ionic substrates. Examples of reactions include superoxide radical chemistry, disproportionation, and C-H and C-O bond activation. This special salt effect is usually quantitative and sometimes catalytic. When compared to other salts, $Na^+PF_6^-$ by far gives the most spectacular results, due to the small size of Na^+ as compared to large organometallic cations.

INTRODUCTION

Since its discovery by Winstein[1], the special salt effect resulting from exchange between two ion pairs has been known to influence reactions between nucleophiles and electrophiles, such as acid-base equilibria, acylation equilibria, E_1/S_N1 competition, reactions of activated sulfoxides, opening of epoxides, electrophilic additions to olefins, aromatic electrophilic substitution, reduction of silanes, formation of carbon-carbon bonds in acidic media and photoinduced electron transfer[2,3].

However, the most spectacular and dramatic special salt effects were found a decade ago in organotransition-metal electron-transfer chemistry[4]. In this area, the special salt effect is usually quantitative in the case of the added $Na^+PF_6^-$ in THF. It can also be catalytic[5]. Even endergonic electron-transfers can be induced quantitatively by $Na^+PF_6^-$. In this article, we will review these results. The understanding of these special salt effects is crucial to our strategies focused on bond activation and formation required for the molecular engineering and synthesis of organometallic molecular trees[5]. Furthermore, salt effects are important in electron-transfer processes such as those involved in molecular activation, material science, electron-transfer-chain catalysis (electrocatalysis) and redox catalysis[6,7]. It is striking that $Na^+PF_6^-$ nearly always gives quantitative reaction changes whereas the effects of other salts are not so marked. This is due to the combination of the sizes of the cations and anions involved in the double ion-pair exchange.

RESULTS AND DISCUSSION

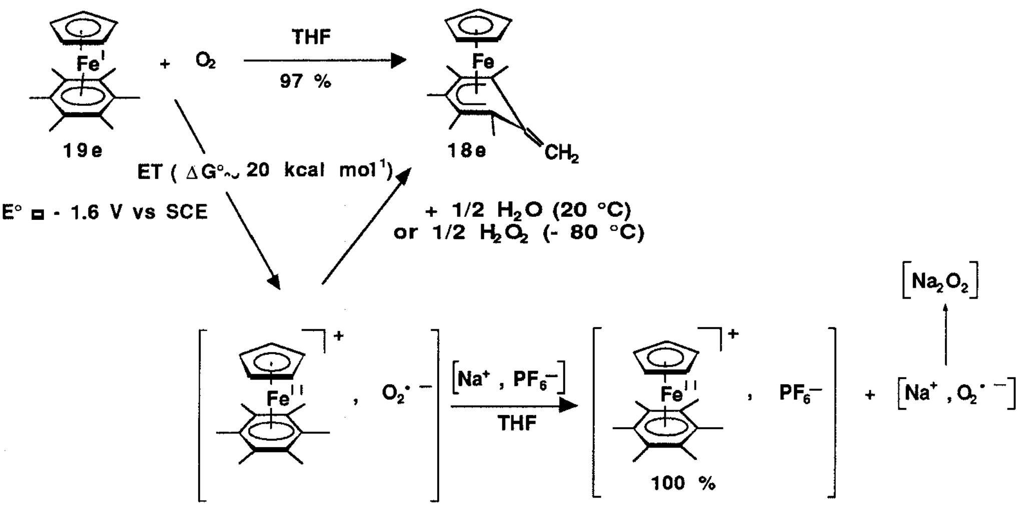
1. Inhibition of the Cage Reactions of Superoxide Radical Anion : $Na^+PF_6^-$ Mimicks Superoxide Dismutase Enzymes

Superoxide radical anion can be easily generated using Fe(I) electron-reservoir sandwich complexes and O_2. The difference in standard redox potentials between the redox systems $O_2^{0/-}$ ($E^0 = -0.7$ V vs SCE in DMF) and $FeCp(C_6Me_6)^{0/+}$ ($E^0 = -1.55$ V vs SCE in DMF) is 0.85 V (20 kcal.mol^{-1}), and thus all allows a very exergonic electron transfer (eq. 1) :

$$[Fe^ICp(C_6Me_6)] + O_2 \rightarrow [Fe^{II}Cp(C_6Me_6)^+, O_2^{\bullet -}] \qquad \text{eq. 1}$$

Actually, the reaction of equation 1 leads to the complex $[Fe^{II}Cp(C_6Me_5CH_2)]$, resulting from a net H-atom abstraction by O_2 from the Fe^I complex. Thus, a cage reaction following electron-transfer is proton transfer (Scheme 1).

The reaction proceeds in 97% yield in pentane or THF. At 20 °C, 1/4 mol H_2O is formed subsequent to cleavage of the O-O bond of O_2 (1/4 mol O_2 is consumed), whereas, at -80 °C, 1/2 mol H_2O_2 is formed from 1/2 mol O_2. However, in the presence of 1 equivalent of $Na^+PF_6^-$ in THF, none of the cyclohexadienyl complex **2** is formed and the precipitate of $\mathbf{1}^+PF_6^-$ is found in quantitative yield as is Na_2O_2 resulting from the Na^+ induced disproportionation of $O_2^{\bullet -}$. Total inhibition of the cage reaction of $O_2^{\bullet -}$ (deprotonation) occurs even at -80 °C. Both the cage reaction and the inhibition reactions proceed in a few seconds. Other salts also partly inhibit the cage deprotonation reactions of $O_2^{\bullet -}$, but not quantitatively (Table I), consistent with the relative sizes of the cations and anions involved in the ion-pair exchange.



Scheme 1

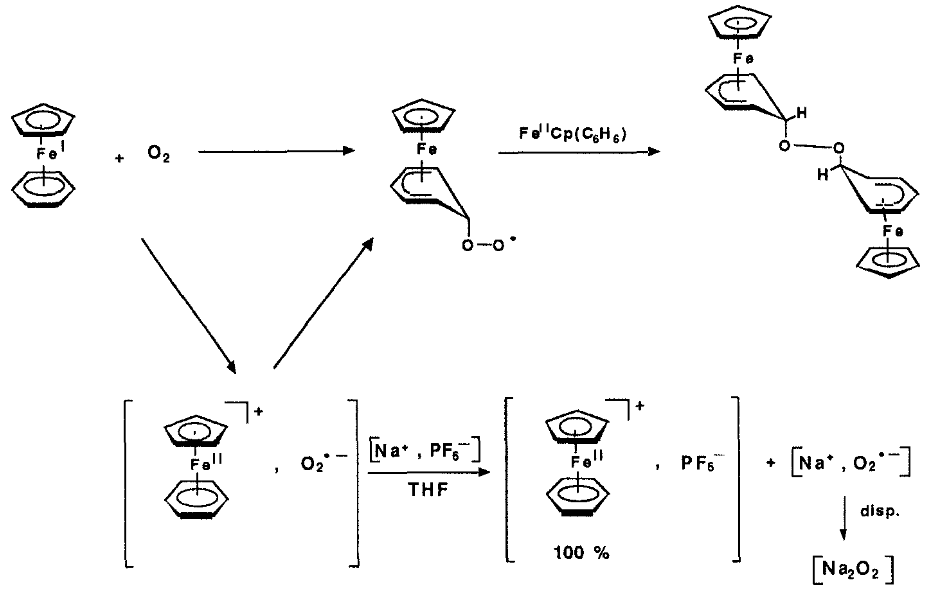
Table I : Salt Effects on the Reactivity of $O_2^{\bullet -}$ as a Base in the Reaction :

$$\underset{A}{CpFe^{I}(C_6Me_6)} \xrightarrow[-\ 80\ °C,\ THF]{O_2} \underset{B}{CpFe^{II}(C_6Me_5CH_2)} + \underset{A^+X^-}{[CpFe^{II}(C_6Me_6)]X^-}$$

Salt M^+X^-	% B	% A^+X^-
none	92	8
$n\text{-}Bu_4N^+PF_6^-$	85	15
$K^+PF_6^-$	45	55
$K^+PF_6^-$ + 18-crown-6	83	17
$Na^+PF_6^-$	0	100
$Na^+BF_4^-$	30	70
Na^+F^-	65	35

[A] = [Salt] = 0.033 M

When no acidic protons are present in the cationic sandwich complex, superoxide reacts as a nucleophile in the cage reaction. Nucleophilic addition of superoxide anion proceeds onto the benzene ligand activated by the FeCp$^+$ moiety. The intermediate peroxy radical produced in this way couples with a starting Fe^I sandwich radical through the benzene ligand of the latter, producing an orange dimer which contains cyclohexadienyl ligands (Scheme 2). Again, this reaction is totally inhibited by one equivalent of $Na^+PF_6^-$, whereas other salts only partially inhibit the cage reaction (Table II)[8]. Similar salt effects were found in the reaction of other 19 and 20 electron complexes with O_2,[9-12] as well as in the reactions of other electron-rich organo-iron compounds with O_2[13].



Scheme 2

TABLE II : Salt Effects on the Reactivity of $O_2^{\bullet -}$ as a Nucleophile in the Reaction :

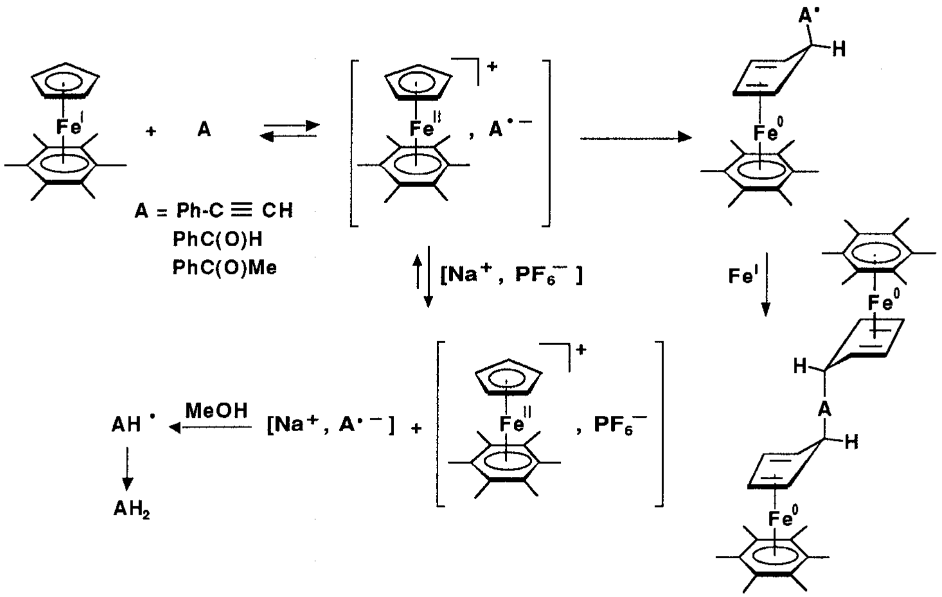
$$\underset{C}{[CpFe^{I}(C_6H_6)]} \xrightarrow[-80\ °C,\ THF]{O_2} \underset{D}{[CpFe^{II}\{\eta^5\text{-}C_6H_6O\text{-}\}]} + \underset{C^+X^-}{[CpFe^{II}(C_6H_6)]X^-}$$

Salt M^+X^-	% D	% C^+X^-
none	100	0
$K^+PF_6^-$	30	60
$K^+PF_6^-$ + 18-crown -6	60	30
$Na^+PF_6^-$	0	100

[C] = [Salt] = 0.067 M

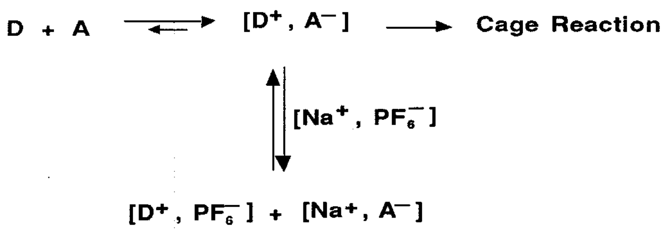
2. Effect of $Na^+PF_6^-$ on the Reduction Chemistry Using Electron-Reservoir Complexes

Electron-reservoir complexes can reduce a number of substrates stoichiometrically or catalytically[6-14]. Not surprisingly, salts have a marked effects on these reactions as well as on electron-transfer chain reactions which are initiated by paramagnetic iron sandwich complexes[15-18]. The reactions proceed with phenylacetylene, benzaldehyde and acetaldehyde (Scheme 3) as indicated above with O_2. In the absence of a salt, nucleophilic addition onto the cyclopentadienyl ligand occurs within the cage subsequent to electron transfer. Orange neutral cyclopentadiene adducts are obtained after coupling with a molecule of Fe^I complex. In the presence of $Na^+PF_6^-$, however, double exchange among the two ion pairs gives the sodium salt of the radical anion of the substrate which is protonated and hydrogenated in the presence of methanol (Scheme 3). Here again, the effect of $Na^+PF_6^-$ is quantitative, no Fe^0 adduct being formed. This reduction chemistry recalls Kagan's reactions using SmI_2[19]. The major difference is that SmI_2 involves both outer-sphere and inner-sphere reduction pathways, whereas the Fe^I complex probably only gives rise to the outer-sphere mechanism.

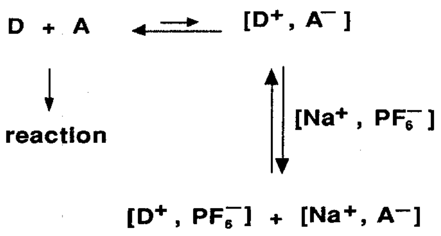


Scheme 3

A very general scheme can be drawn to account for the reduction of a number of substrates in which the electron transfer is exergonic (Scheme 4). In the case of endergonic electron-transfer reactions, competition occurs before electron transfer with a reaction of A or D (Scheme 5).



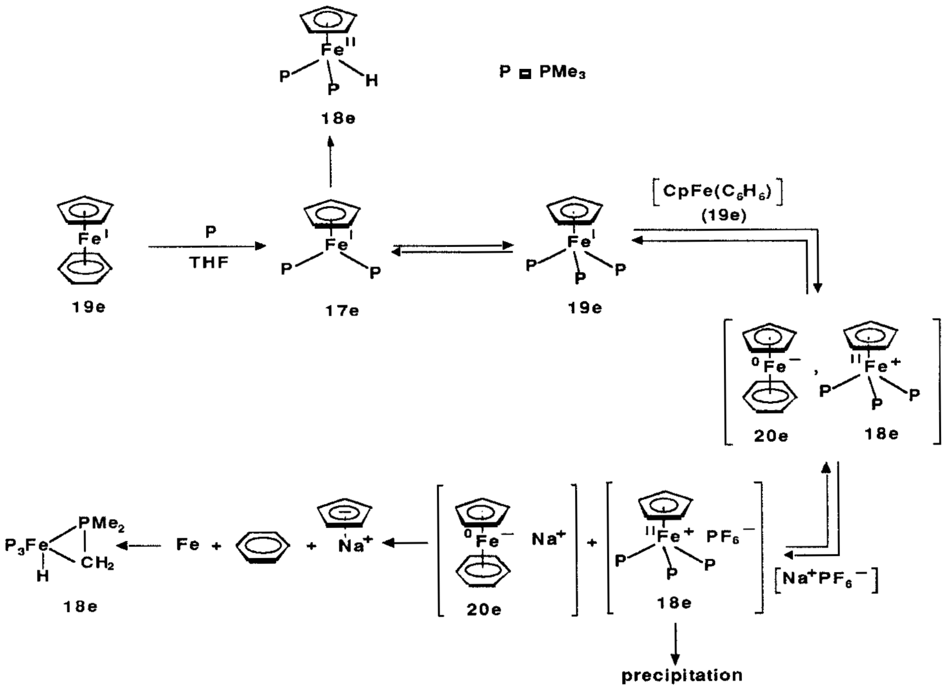
Scheme 4



Scheme 5

3. Induction of Endergonic Electron-Transfer Reactions by $Na^+PF_6^-$

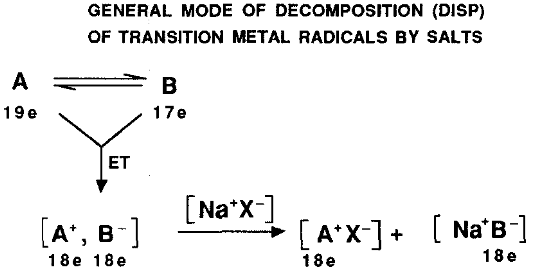
The driving force for the endergonic electron transfer of Scheme 5 is provided by the differing stabilities or by the differing reaction rates between the sodium salt $[Na^+A^-]$ and the organometallic ion pair $[D^+A^-]$. The latter always reacts much more slowly if D^+ is a large organometallic cation.



Scheme 6

An illustration of this principle is provided in the reactions of $[Fe^ICp(C_6H_5R)]$, (R = H or CH_3) with phosphorus ligands such as PMe_3 or $P(OMe)_3$. These reactions proceed in various solvents at -10 °C to give the 17e species $[Fe^ICp(PR_3)_2]$, (Scheme 6) which is generated by loss of the benzene ligand. With R = Ph, the 17e species can be characterized by the triplet in the ESR spectrum resulting from coupling of the iron-centered spin with the two phosphorus atoms. If R is smaller (CH_3 or OCH_3), the $[Fe^ICp(PR_3)_2]$ (17e) and $[Fe^ICp(PR_3)_3]$ (19e) rapidly interconvert. Depending on the reaction medium, reactions proceeding through the 17e species or through the 19e species are observed. In the absence of $Na^+PF_6^-$ or of an acceptor, the 17e species reacts by H-atom abstraction from the medium or by the radical Arbuzov reaction (in the case R = OMe). In principle, the competitive reaction is the reduction of the Fe^I sandwich complex by [$Fe^ICp(PR_3)_3$]. However, the ion-pair produced has a large cation and a large anion so that its decomposition is slow. In the presence of $Na^+PF_6^-$, double ion pair exchange occurs very rapidly to give the much more kinetically unstable ion pair [Na^+, $FeCp(C_6H_6)^-$] whose decomposition displaces the electron-transfer equilibrium. The endergonicity of the electron-transfer step is 0.1V for R = Me and reaches 0.5 V for R = OMe. (Scheme 6)[21].

We have also found this type of salt induced decomposition of organotransition-metal radicals in other cases[20], so a simple general scheme of salt induced disproportionation for organotransition-metal radicals can be drawn (Scheme 7).


GENERAL MODE OF DECOMPOSITION (DISP) OF TRANSITION METAL RADICALS BY SALTS

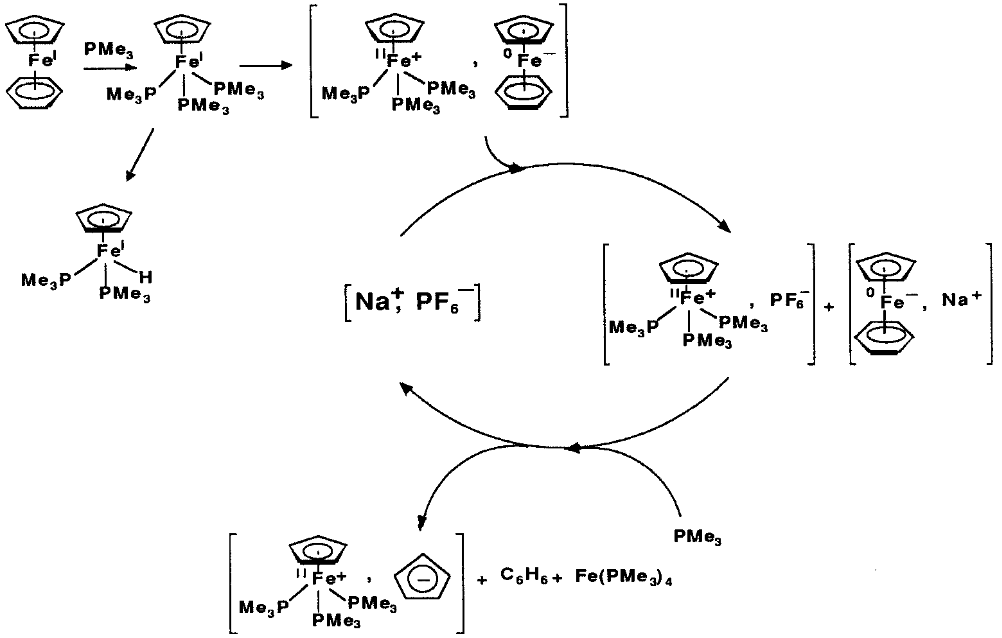
Scheme 7

4. Catalysis of Electron-Transfer Reactions by $Na^+PF_6^-$

The special salt effect described above involves a stoichiometric quantity of salt due to the precipitation from THF of at least one reaction products containing PF_6^-, the anion of the added salt (in the case discussed in § 1, Na_2O_2 also precipitates). We have attempted to work in a solvent which would not allow precipitation of any reaction products in the disproportionation system described in § 3 for two reasons. The first one was to check that the additional driving force gained from the precipitation is not the major, decisive factor of the special salt effects (which it should not be). The second one was to investigate the extent to which the salt could be used catalytically.

The reaction between [$Fe^ICp(C_6H_6)$] and PMe_3 was carried out in a 1:1 mixture of THF and MeCN, in which the products of the reaction carried out in the presence of $Na^+PF_6^-$ are soluble. The reaction products resulting from the salt-induced disproportionation were formed quantitatively even when the amount of $Na^+PF_6^-$ was as low as 0.1 equivalent. Thus, this 0.1 equivalent of $Na^+PF_6^-$ is able to switch the reaction from a radical type (quantitative H-atom abstraction), in the absence of salt, to quantitative disproportionation (Scheme 8).

In this context, we noticed that the parent [$Fe^ICp(C_6H_6)$] complex had been reported by Russian authors to be unstable and to decompose to ferrocene, iron and benzene[22] (the disproportionation products). We envisaged that a Na^+ salt might have been present in the THF solution. We could indeed observe the same result when [$Fe^ICp(C_6H_6)$] was allowed to react in THF with 0.1 equiv. of $Na^+PF_6^-$. One should recall here that the



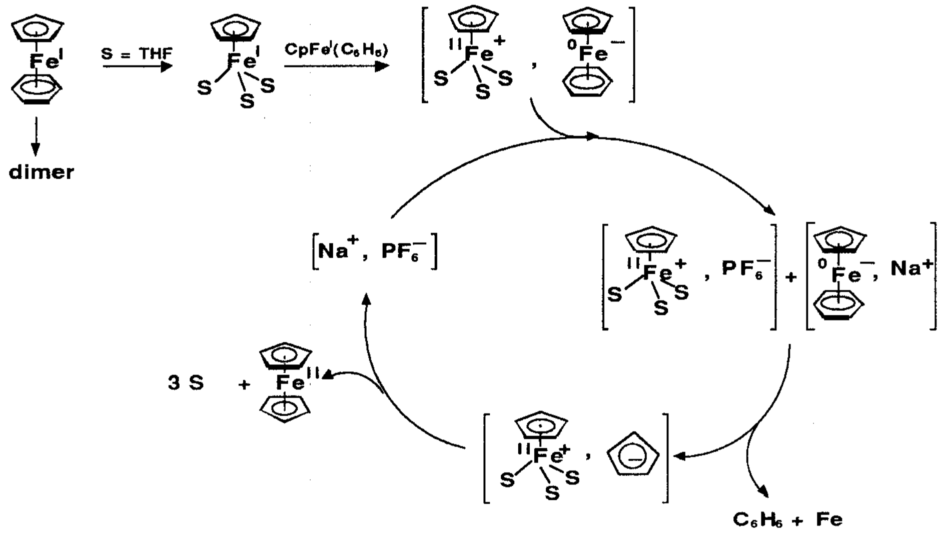
Scheme 8

[$Fe^ICp(arene)$] complexes are prepared by Na/Hg reduction of the 18e cationic precursors as BF_4^- or PF_6^- salts[23,25]. Thus the reaction produces $Na^+BF_4^-$ or $Na^+PF_6^-$ which then contaminates the Fe^I complex if proper care is not exercised (eq. 2)

$$[FeCp(arene)]^+PF_6^- + Na/Hg \xrightarrow{THF} [Fe^ICp(arene)] + Na^+PF_6^- + Hg \qquad \text{(eq. 2)}$$

Hence, in another experiment, we carried out the same reaction with a sample of [$Fe^ICp(C_6H_6)$] that had been extracted using only pentane or pentane + 10% toluene. $Na^+PF_6^-$ is insoluble in these solvents. The reaction of a thus purified sample of [$Fe^ICp(C_6H_6)$] in THF at 20 °C does not give any disproportionation product, but only the dimer, which was also known to form in pentane[23,24] (equation 2). Thus, it is probable that the Russian group overlooked the presence of a Na^+ salt and its effect in their study of the disproportionation reaction of the Fe^I complex.

The catalysis of disproportionation of [$Fe^ICp(C_6H_6)$] by 0.1 equivalent of $Na^+PF_6^-$ can now be rationalized as shown in Scheme 9, analogous to Scheme 8. $[Fe^{II}CpS_3]^+$ $C_5H_5^-$ is not stable with S = THF and $C_5H_5^-$ further displaces the three S ligands to produce ferrocene[4].

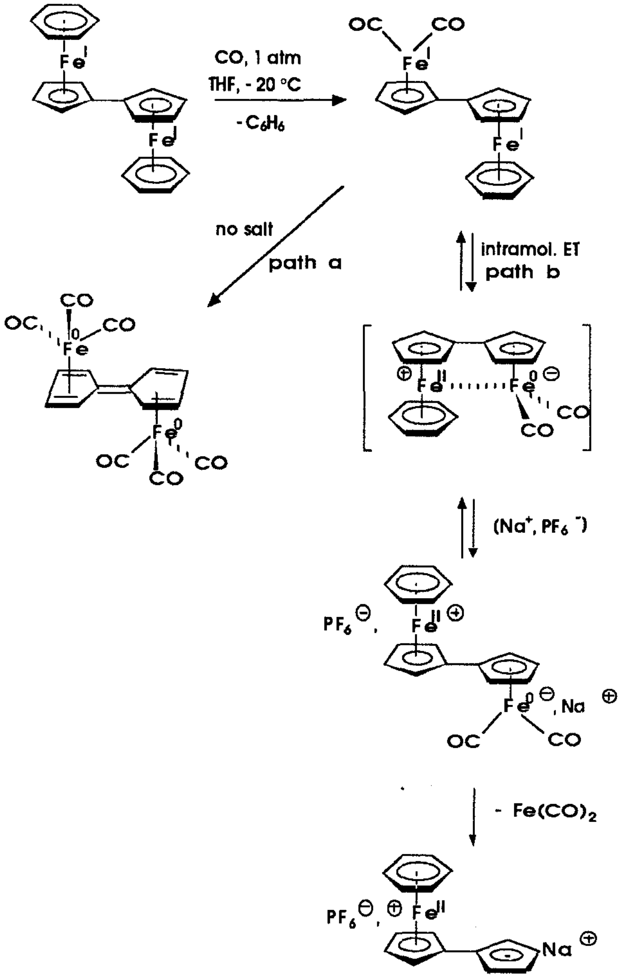


Scheme 9

5. Induction of an Intramolecular Electron-Transfer Reaction by $Na^+PF_6^-$

An intramolecular version of the double ion-pair exchange allows the charges of zwitterions to be separated. The consequences can include the destabilization and decomposition of these zwitterions. Thus, $Na^+PF_6^-$ is of great synthetic use to control the reactivity of odd-electron binuclear systems such as the following, described in Scheme 10. In the absence of a salt, the Fe^IFe^I "biradical" reacts with CO to give substitution of the two benzene ligands by six CO ligands. This path competes with intramolecular electron transfer between the two iron radical centers after the first benzene substitution by two CO ligands which is roughly isoergonic, but the zwitterion is stabilized as shown in Scheme 10. In the presence of $Na^+PF_6^-$, however, double ion-pair exchange leads to charge dislocation and decomposition of the anionic fragment ; this drives the competition to the formation of the zwitterionic reaction product[27].

Note that, if the Fe^IFe^I complex reacts with PMe_3, both the substituted and entering ligands are electron-rich, which does not allow intramolecular electron transfer to occur. In this case, only intermolecular electron-transfer is found, as in the mononuclear complex whose chemistry is described in Scheme 6[27,28]. In the absence of a salt, the radical reaction observed is simply intramolecular homo-coupling of the two iron centers.



Scheme 10

6. The Influence of Salts on the Reactivity of Ionic Complexes

All the systems described in § 1-5 involve reactions of neutral substrates. A special salt effect can also be found to be dramatic in the reactions of ionic substrates[2,3]. For instance, the peralkylation of polymethyl arene ligands in $[\mathrm{FeCp(arene)}]^+$ complexes[29] is of great synthetic use (eq. 3)[30-37]. It can be inhibited by the presence of one equivalent of $K^+PF_6^-$, a feature rationalized by the fact that the equilibrium producing the reactive cage ion pair is displaced in the wrong direction by the added salt (eq. 4).

$$[\mathrm{FeCp(C_6Me_6)}]^+\mathrm{PF_6}^- \xrightarrow[\text{THF or DME}]{\substack{\text{KOR, RX}\\ \text{R=H or tBu}}} \begin{array}{c}[\mathrm{FeCp(C_6CH_2R)_6}]^+\mathrm{PF_6}^-\\ \text{R = alkyl, allyl, benzyl}\end{array} \qquad \text{(eq. 3)}$$

$$[FeCp(C_6Me_6)^+, PF_6^-] + [K^+,OR^-] \rightleftarrows [FeCp(C_6Me_6)^+, OR^-] + [K^+,PF_6^-] \quad \text{(eq. 4)}$$

$$\downarrow$$

deprotonation

There are other relevant cases in which the special salt effect plays a major role[33-35] ; $Na^+PF_6^-$ is most often the ideal salt in terms of the sizes of its ions. In some instances, $Na^+ClO_4^-$ has been used[34] but, due to the danger of explosions of the latter and to the similar function of PF_6^- and ClO_4^-, $Na^+PF_6^-$ should always been used instead of the perchlorate salt.

CONCLUSION

The presence $Na^+PF_6^-$ totally switches the reactivity in molecular transition metal chemistry, an area in which the special salt effect is much more marked than in organic reactions. This special salt effect of $Na^+PF_6^-$ occurs on reactions between neutral substrates as well as on reactions between ionic substrates. It is especially spectacular in electron-transfer reactions between a neutral donor and a neutral acceptor in THF since the tight ion pair formed is dislocated by the $Na^+PF_6^-$ ion pair. Depending on whether the electron-transfer reaction is exergonic or endergonic, the special salt effect intervenes in competition with a reaction either proceeding after electron transfer or before it. It has been shown that, if the solvent is chosen so that the reaction medium remains homogeneous, the salt can be used in catalytic amounts to induce the electron-transfer reactions.

It is remarkable that $Na^+PF_6^-$ is the best choice to provide a quantitative special salt effect whereas other salts with a larger cation and/or a smaller anion are not as efficient as $Na^+PF_6^-$ (cf. Tables I and II). This is attributable to the small size of Na^+. In electron-transfer reactions, the electron-rich organometallic substrate acts as a reductant and forms a large cation (eq. 5) :

$$D + A \rightarrow [D^+, A^-] \xrightleftharpoons{[Na^+,PF_6^-]} [D^+PF_6^-] + [Na^+, A^-] \qquad \text{(eq. 5)}$$

Thus, the replacement of a large organometallic cation by the small Na^+ cation considerably changes the thermodynamics and the kinetics of the ion pairs. In conclusion, special salt effects should take an important part in engineering synthetic strategies when classical routes fail.

Acknowledgement

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References

1. Winstein, S. ; Clippinger, E. ; Fainberg, A.H. ; Heck, R. ; Robinson, G.C. *J. Am. Chem. Soc.* 1956, *78*, 328.
2. For a recent review on the special salt effect see : Loupy, A. ; Tchoubar, B. ; Astruc, D. *Chem. Rev.* 1992, *92*, 1141.
3. For an excellent book on salt effects, see Loupy, A. ; Tchoubar, B. *"Salts Effects in Organic and Organometallic Chemistry"*, VCH, Weinheim, 1992.
4. Hamon, J.-R. ; Astruc, D. *J. Am. Chem. Soc.* 1983, *105*, 5951.
5. Ruiz, J. ; Lacoste, M. ; Astruc, D. *J. Am. Chem. Soc.* 1990, *112*, 5471.
6. Astruc, D. in *"Mechanisms and Processes in Molecular Chemistry"* Astruc, D. Ed., *New J. Chem.* 1992, *16*, 305.
7. Lacoste, M. ; Desbois, M.-H. ; Astruc, D. *Nouv. J. Chim.* 1987, 561.
8. Hamon, J.-R. ; Astruc, D. *Organometallics* 1989, *8*, 2243.
9. Madonik, A.M. ; Astruc, D. *J. Am. Chem. Soc.* 1984, *106*, 2437.
10. Astruc, D. ; Mandon, D. ; Madonik, A.M. ; Michaud, P. ; Ardoin, N. ; Varret, F. *Organometallics* 1990, *9*, 2155.
11. Astruc, D. *Topics Curr. Chem.* 1991, *160*, 47.
12. Astruc, D. *Synlett* 1991, 369.
13. Roger, C. ; Hamon, J.-R. ; Toupet, L. ; Rabaâ, H. ; Saillard, J.-Y. ; Hamon, J.-P. ; Lapinte, C. *Organometallics* 1991, *10*, 1045.
14. Astruc, D. *Acc. Chem. Res.* 1986, *19*, 377.
15. Desbois, M.-H. ; Astruc, D. *New. J. Chem.* 1989, *13*, 595.
16. Astruc, D. *Angew. Chem. Int. Ed. Engl.* 1988, *27*, 643.
17. Verpeaux, J.-N. ; Desbois, M.-H. ; Madonik, A.M. ; Amatore, C. ; Astruc, D. *Organometallics* 1990, *9*, 630.
18. Astruc, D. *Acc. Chem. Res.* 1991, *24*, 36.
19. **a)** Kagan, H.B. ; Namy, J.L. *Tetrahedron Report N° 213, Tetrahedron* 1980, *42*, 6573 ; **b)** Kagan, H.B. in *'Mechanisms and Processes in Molecular Chemistry"* Astruc, D. Ed. *New. J. Chem.* 1992, *16*, 89.
20. Desbois-Delville, M.-H. ; Varret, F. ; Astruc, D. to be submitted for publication.
21. Ruiz, J. ; Lacoste, M. ; Astruc, D. *J. Chem. Soc., Chem. Commun.* 1989, 813.
22. Nesmeyanov, A.N. ; Vol'kenau, N.A. ; Shilovtseva, L.S. *Isz. Akad. Nauk. SSSR, Ser. Khim.* 1969, 725.
23. Nesmeyanov, A.N. ; Vol'kenau, N.A. ; Shilovtseva, L.S. ; Petrakova, V.A. *J. Organomet. Chem.* 1973, *61*, 329.
24. Hamon, J.-R. ; Astruc, D. ; Michaud, P. *J. Am. Chem. Soc.* 1981, *103*, 758.
25. Astruc, D. *Tetrahedron Report N° 157, Tetrahedron* 1983, *39*, 4027.
26. Astruc, D. ; Hamon, J.-R. ; Lacoste, M. ; Desbois, M.-H. ; Madonik, A.M. ; Román, E. in *Organomet. Syntheses* ; King, R.B. Ed., Elsevier, New York 1988, Vol 4, pp 172-187.
27. Delville, M.-H. ; Lacoste, M. ; Astruc, D. *J. Am. Chem. Soc.* 1992, *114*, 8310.
28. Lacoste, M. ; Astruc, D. ; Garland, M.-J. ; Varret, F. *Organometallics* 1988, *7*, 2253.
29. Astruc, D. ; Hamon, J.-R. *et al. J. Am. Chem. Soc.* 1979, *101*, 5445.
30. Moulines, F. ; Astruc, D. *Angew. Chem. Int. Ed. Engl.* 1988, *100*, 1394.
31. Fillaut, J.-L. ; Boese, R. ; Astruc, D. *Synlett* 1992, 55.
32. Moulines, F. ; Djakovitch, L. ; Fillaut, J.-L. ; Astruc, D. ; *Synlett* 1992, 57.
33. Lapinte, C. ; Catheline, D. ; Astruc, D. *Organometallics* 1988, *7*, 1683.
34. Barrat, D.S. ; Cole-Hamilton, D.J. *J. Chem. Soc., Chem. Commun.* 1985, 1559.
35. Moulines, F. ; Djakovitch, L. ; Delville-Desbois, M.-H. ; Astruc, D., to be published.