4. 2,3-Dihydrobenzofuran (10). Since 5-membered rings are generally more planar than 6-membered rings it seemed probable that θ would be decreased by reducing the heterocyclic ring to this size. In the one phenol of this class that we have been able to examine,[16] i.e., **10**, the reactivity toward peroxyl radicals is enhanced by a factor of 1.66 relative to **1** or 1.43 relative to **2**. This enhancement in k_1 is larger than the factor of 1.1, which can be calculated assuming a $\cos^2 \theta$ dependence for orbital overlap with $\theta = 0°$ and 16° for **10** and **2**, respectively. This is a surprising result, which we are investigating further, but it remains to be seen whether an analogue of **10** having appropriate lipophilicity would show greater Vitamin E activity than α-tocopherol.

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Registry No. 1, 86646-82-4; **2**, 950-99-2; **3**, 21704-70-1; **4**, 56305-04-5; **5**, 86646-83-5; **6**, 86646-84-6; **7**, 50869-01-7; **8**, 50869-02-8; **9**, 86646-85-7; **10**, 86646-86-8.

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[16] Crystals suitable for X-ray analysis could not be obtained.

Dramatic Salt Effects on the Basic and Nucleophilic Properties of Superoxide Radical Anion Generated from O_2 and Iron(I) "Electron-Reservoir Complexes"[1]

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The superoxide radical anion has attracted considerable attention recently because of its role in the degradation of red cells, membranes, granulocytes, and bacteria.[2] In particular its properties as a base, nucleophile, ligand, reducing agent, and its photon- and transition-metal-induced reduction and disproportionation have been studied.[3] In these investigations, chemists were compelled to use KO_2 in Me_2SO or in THF with stoichiometric 18-crown-6 because of the insolubility of superoxide salts; the only alternative was electrogeneration of $O_2^{-}\cdot$ in pyridine or DMF. Our approach has consisted of generating $O_2^{-}\cdot$ from dioxygen or air and neutral Fe^I "electron–reservoir complexes"[4,5] under mild conditions. A spectacular H atom abstraction observed in such systems is the result of rapid outer-sphere electron transfer to O_2 followed by deprotonation by $O_2^{-}\cdot$ in the cage (eq 1).[5]

$$\underset{\mathbf{1}}{CpFe^I(\eta^6\text{-}C_6Me_6)} \xrightarrow{O_2 \text{ or air}} \underset{\mathbf{2}}{CpFe^{II}(\eta^5\text{-}C_6Me_5CH_2)} \quad (1)$$

Table I. Salt Effect on the Reactivity of $O_2^{-}\cdot$ as a Base in the Reaction I $\xrightarrow[-80\ °C,\ THF]{O_2}$ 2 (1)[a]

M^+X^-[c]	2	1^+X^-
without	92[b]	8[b]
$n\text{-}Bu_4N^+PF_6^-$	85	15
$K^+PF_6^-$	45	55
$K^+PF_6^-$ + 18–6 (stoich)	83	17
$Na^+PF_6^-$	0	100
$Na^+BF_4^-$	30	70
Na^+F^-	65	35

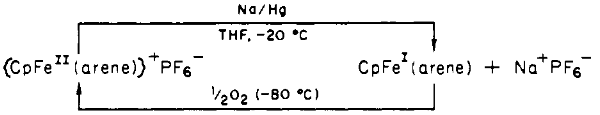
[a] See also eq 4 and 6. Percent of 2 and 1^+X^- determined by weight (reactions are immediate). [b] At 20 °C, the crude yields are 2, 97%; $I^+PF_6^-$, 3%.[5a-c] [c] Concentrations of both I and the salt in THF (30 mL) are 0.033 mol L^{-1}. With other $CpFe^I$(arene) complexes (arene = toluene, mesitylene, pentamethylbenzene, ethylbenzene, fluorene), analogues of 2 are not formed in the presence of 1 equiv of $Na^+PF_6^-$ under identical conditions [90–100% yield of $(CpFe(arene))^+PF_6^-$].

We also know that in the absence of benzylic hydrogens, formation of a neutral peroxide occurs,[6] although the mechanism was unknown.

$$2\underset{\mathbf{3}}{CpFe^I(\eta^6\text{-}C_6H_6)} + O_2 \xrightarrow[-80\ °C]{toluene} \underset{\mathbf{4}}{[CpFe^{II}(\eta^5\text{-}C_6H_6O\text{-})]_2} \quad (2)$$

We now wish to report salt effects on the reactivity of $O_2^{-}\cdot$ generated in these systems from O_2 or air and Fe^I complexes.

The starting point for these findings was an attempt to generalize the benzylic C–H activation reaction of eq 1 to other arene Fe^I complexes[7] (arene = toluene, ethylbenzene, mesitylene, pentamethylbenzene, fluorene). The major problem was that $CpFe^I$(arene) complexes are unstable above −15 °C in THF or DME solution in which they are synthesized by Na/Hg reduction of their precursor 18-electron d^6 PF_6^- salts. Thus $^1/_2$ mol of O_2 was added at −80 °C to such forest-green solutions subsequent to synthesis at −20 °C (1 h) and filtration by canula. A yellow precipitate and a colorless solution were always obtained by this procedure whatever the arene ligand in the sandwich complex and in particular whether or not it bears benzylic hydrogen(s). $CpFe^+(arene)PF_6^-$ can be extracted from the precipitate with CH_2Cl_2, leaving white insoluble Na_2O_2 characterized by the peroxide stretch at 805 cm^{-1} in the IR spectra (eq 3). On the other hand, if $NaPF_6$ is eliminated from the THF solution[9] prior to the addition of O_2, no precipitate is formed; the stoichiometry in O_2 remains $^1/_2$ mol and the solution turns dark red if a benzylic hydrogen is present on the arene and orange otherwise. The



(3)

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[7] For syntheses of unstable $CpFe^I$(arene) complexes, see ref 4, 5d, and: (a) Nesmeyanov, A. N.; Vol'kenau, N. A.; Shilovtseva, L. S.; Petrakova, V. A. *J. Organomet. Chem.* **1973**, *61*, 329–335. (b) Nesmeyanov, A. N.; Sinitsijna, N. A.; Kotova, L. S.; Kolesov, V. S.; Cizoi, V. F.; Vol'kenau, N. A. *Dokl. Akad. Nauk SSSR* **1978**, *242*, 1356–1358. (c) Nesmeyanov, A. N.; Vol'kenau, N. A.; Kotova, L. S. *Koord. Khim.* **1978**, *4*, 1699–1704.

[8] $CpFe^+(arene)PF_6^-$ salts were characterized by elemental analyses and IR and ^1H NMR spectra by comparison with authentic samples. See for example: (a) Khand, I. U.; Pauson, P. L.; Watts, W. E. *J. Chem. Soc. C* **1968**, 2257–2260, 2261–2264. (b) Astruc, D.; Dabard, R. *Bull. Soc. Chim. Fr.* **1975**, 2571–2574. (c) Astruc, D. *Tetrahedron*, in press.

[9] The unstable $CpFe^I$(arene) complex can be isolated at low temperature and dissolved in THF;[7] alternatively $NaPF_6$ can be removed by addition of excess cold pentane, followed by filtration, removal of solvents in vacuo, and addition of THF.

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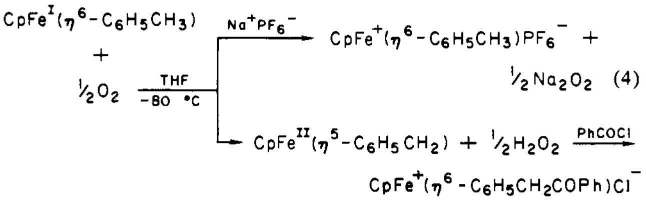
Table II. Salt Effect on the Reactivity of $O_2^{-}\cdot$ as a Nucleophile in the Reaction 3 $\xrightarrow[-80\ °C,\ THF]{O_2}$ 4 (2)[a]

M^+X^- [b]	4	$3^+PF_6^-$
without	100	0
$K^+PF_6^-$ + 18-6 (stoich)	60	40
$K^+PF_6^-$	30	70
$Na^+PF_6^-$	0	100

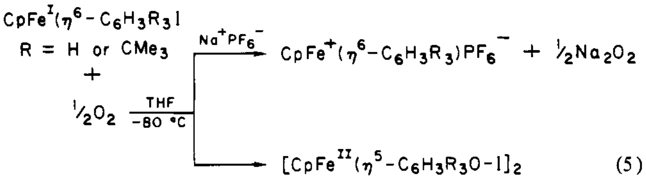
[a] See also eq 5 and 6. Percent of 4 and $3^+PF_6^-$ determined by weight (reactions are immediate). [b] Concentrations of both 3 and the salt in THF (30 mL) are 0.067 mol L^{-1}; $Na^+PF_6^-$ produces the same salt effect in DME.

dark-red C–H activation products are thermally unstable above -50 °C but reaction with PhCOCl at -80 °C (3 h) gives the benzoylation product even in the case of the most unstable parent complex $CpFe^{II}(\eta^5\text{-}C_6H_5{=}CH_2)$ (eq 4). In this later case, a

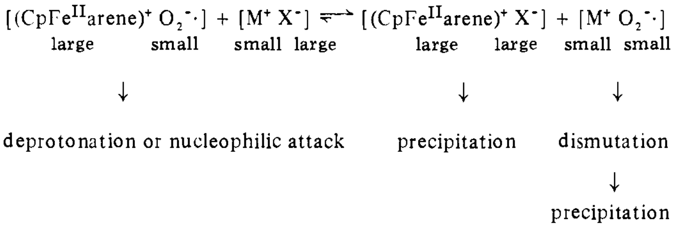


{^1H}^{13}C NMR spectrum recorded at -80 °C subsequent to reaction between $^1/_2$ mol of O_2 and $CpFe^I(C_6H_5CH_3)$ in toluene-d_8 at -80 °C and filtration reveals the presence of the uncoordinated cyclohexadienyl carbon (δ 135 vs. Me_4Si).[10]

Orange dimeric peroxides[6,11] are characterized in the cases of the reactions of $CpFe^I(C_6H_6)$ and $CpFe^I(1,3,5\text{-}t\text{-}Bu_3C_6H_3)$ and $^1/_2$ mol of O_2 in the absence of $NaPF_6$ (-80 °C, fast) (eq 5). Thus



it turns out that a stoichiometric amount of $NaPF_6$ in THF solution changes the course of the reactions in the case of benzylic C–H activation as well as in the case of the formation of dimeric neutral peroxides. If only $^1/_2$ mol of $NaPF_6$ is added to a THF solution of **1**, addition of $^1/_2$ mol of O_2 at -80 °C leads to the formation of $^1/_2$ mol of **2** and $^1/_2$ mol of $1^+\ PF_6^-$ + $^1/_4$ mol of Na_2O_2. This salt effect[12] is confirmed by using other salts such as KPF_6, $n\text{-}Bu_4NPF_6$, $NaBF_4$, and NaF (Table I) in the reaction of O_2 with **1**. Whereas the salt effect is "quantitative" with $NaPF_6$, it decreases as the size of the cation increases and as the size of the anion decreases. Similar observations were obtained in the formation of **4** from **3** (Table II). Along this line, the salt effects on both reactions are inhibited by the presence of the suitable crown ether (18-6 with K^+). Note that since 18-crown-6 is required in reactions of KO_2 in THF, salt effects could not be observed before this strategy to generate $O_2^{-}\cdot$ was developed. These data are obviously in agreement with $O_2^{-}\cdot$ as intermediate in both the C–H activation and the formation of dimeric peroxide. This conclusion is also supported by the characteristic EPR spectra



(6)

of $O_2^{-}\cdot$ in frozen THF solution in the presence or absence of $NaPF_6$ and/or of benzylic hydrogen(s).[13]

The present observations indicate that ion exchange due to their relative sizes occurs in the ion pairs as shown in eq 6, this process being faster than reaction of $O_2^{-}\cdot$ in the cage.

Additional driving forces shifting this equilibrium to the right are (i) the alkali-cation-induced disproportionation of superoxide to peroxide[14] and (ii) the precipitation of both Na_2O_2 and the organometallic PF_6 salt. However the competition between the interaction of the alkali cation with its counteranion and with $O_2^{-}\cdot$ is the major factor in view of the considerable variation of salt effects obtained upon changing either the alkali cation or its counteranion (Tables I and II).

Acknowledgment. We are grateful to Dr. Bianca Tchoubar for invaluable discussions and to the CNRS for financial support (ATP No. 9812).

Registry No. 1, 70414-92-5; **2**, 70414-93-6; **3**, 51812-05-6; 4, 83617-47-4; O_2, 7782-44-7; $O_2^{-}\cdot$, 11062-77-4; $n\text{-}Bu_4N^+PF_6^-$, 109-63-5; $K^+PF_6^-$, 17084-13-8; 18-crown-6, 17455-13-9; $Na^+PF_6^-$, 21324-39-0; $Na^+BF_4^-$, 13755-29-8; Na^+F^-, 7681-49-4; $CpFe^I$(toluene), 69022-30-6; $CpFe^I$(mesitylene), 51812-08-9; $CpFe^I$(pentamethylbenzene), 76747-94-9; $CpFe^I$(ethylbenzene), 78230-46-3; $CpFe^I$(fluorene), 69022-32-8; $CpFe^+(\eta^6\text{-}C_6H_5CH_2COPh)PF_6^-$, 86584-12-5; $[CpFe(\eta^5\text{-}C_6H_3(t\text{-}Bu)_3O)]_2$, 86584-13-6; $CpFe^I(\eta^6\text{-}C_6H_3(t\text{-}Bu)_3)$, 83528-72-7.

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[10] ^{13}C NMR data for $CpFe^{II}(\eta^5\text{-}C_6H_5{=}CH_2)$ ($C_6D_5CD_3$, -80 °C) 134.8 (C uncoordinated), 91.4 (*p*-C), 80.6 (*m*-C), 52.5 (*o*-C), 72.5 (Cp), 73.2 (CH_2). $CpFe^+(\eta^6\text{-}C_6H_5CH_2COPh)PF_6^-$ ^1H NMR (CD_3COCD_3) 7.70 (m, Ph, 5 H), 6.50 (s, C_6H_5, 5 H), 5.26 (s, Cp, 5 H), 4.86 (s, CH_2, 2 H); ^{13}C NMR (CD_3CN) 196.7 (CO), 137.3, 135.2, 131.0, 129.8 (Ph), 101.6 (C quaternary C_6H_5), 91.2, 90.5, 90.0 (*p*-, *m*-, *o*-, C_6H_5), 41.7 (CH_2), 78.8 (Cp).

[11] $[CpFe(\eta^5\text{-}C_6H_6O\text{–})]_2$ ^{13}C NMR (C_6D_6) 72.8 (Cp), 79.8 (*p*-C), 77.9 (*m*-C), 73.3 (sp^3C), 37.1 (*o*-C). $[CpFe(\eta^5\text{-}C_6H_3Bu_3{}^tO\text{–})]_2$ ^1H NMR (C_6D_6) 4.10 (s, Cp, 5 H), 5.43 (s, *m*-H, 2 H), 3.92 (s, CHO, 1 H), 1.55 (s, CH_3, 18 H), 1.50 (s, CH_3, 9 H); ^{13}C NMR (C_6D_6, 15 °C) 74.9 (Cp), 88.0 (*p*-C), 77.9 (*m*-C), 53.9 (*o*-C), 37.9 (*p*-*C*(CH_3)$_3$), 37.6 (*o*-*C*(CH_3)$_3$), 74.7 (sp^3C), 37.9, 37.6 (C(CH_3)$_3$).

[12] For useful discussions of salt effects, see: Gordon, J. E. "The Organic Chemistry of Electrolyte Solutions"; Wiley: New York, 1975.

[13] O_2 was allowed to diffuse slowly into EPR tubes containing frozen THF or DME solutions of the $CpFe^I$ (arene) complexes at 173–180 K (arene = C_6H_6, $C_6H_5CH_3$, $C_6(CH_3)_6$) in the presence or absence of $Na^+PF_6^-$. In all these cases, the spectrum of $O_2^{-}\cdot$ was obtained (77 K, $g_\parallel = 2.091$, $g_\perp = 2.005$). See also ref 3b and 5c.

[14] It is known that disproportionation of superoxide radical anion to peroxide is catalyzed by protons or transition-metal ions, as, for instance, in superoxide dismutase (SOD).[2c,3] We are not aware of precedents indicating that alkali cations can also effect this process, but we propose that this is so in our system. Alternatively, $O_2^{-}\cdot$ could be reduced by the Fe^I complex, a thermodynamically unfavored process that would require an overpotential of ca. 0.6 V.

Multiple-State Emission and Intramolecular Electron-Transfer Quenching in Rhenium(I) Bipyridine Based Chromophore–Quencher Complexes

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Electron-transfer processes involving excited-state quenching in which "electron–electron hole separation" is achieved are an important initial step in many redox photosensitization schemes[1]

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