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## Salt Effects Resulting from Exchange between Two Ion Pairs and Their Crucial Role in Reaction Pathways

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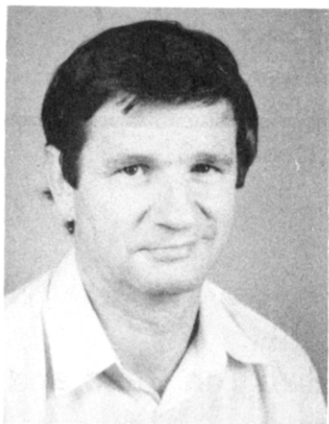
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### I. Introduction

#### A. Scope

Ion pairing is an essential feature of the medium-dependent reactivity in molecular chemistry. In particular the presence of a salt in a reaction medium involving an ion pair brings about a second ion pair which dramatically changes the course of the reaction subsequent to exchange between the two ion pairs. This "special salt effect" concerns all the areas of molecular chemistry from organic to inorganic. We will cover here two broad classes of reactions: (i) between nucleophiles and electrophiles and (ii) electron transfer (ET) including photoinduced and radiolytic ET. Given the ability of transition metals to change redox states, inorganic and organometallic chemistry are deeply

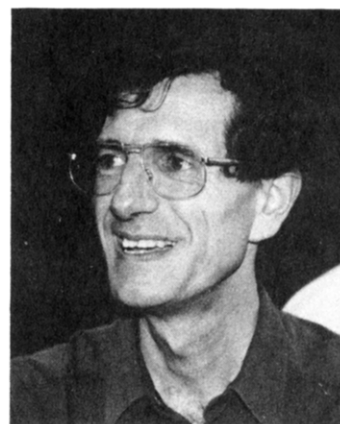


André Loupy, Directeur de Recherches in the Centre National de la Recherche Scientifique (CNRS), was born in Paris in 1945. He studied in Paris-Sud University from which he also received his "Thèse d'Etat" in 1975 under the direction of J. Seyden-Penne, in Thiais. After postdoctoral research with Nguyen Trong Anh (Orsay) involving theoretical chemistry, he moved to Orsay in 1982 at the creation of the "Laboratoire des Réactions Sélectives Sur Supports" (Dir.: Professor G. Bram). His research field is dealing with solvent-free synthesis, with special interest for supported reactions, phase transfer catalysis, salt effects and microwave activation.



Blanka Tchoubar was born in Kharlov (Ukraine) in 1910 and moved to Paris at the age of 14. Like many Russian emigrants, she first studied at the Ecole Russe on Dr. Blanche Street where her teacher, to whom she later said she owed her vocation, was Miss Chamier, a collaborator of Marie Curie. After her "Licence es Science" (1931), she worked on the reaction of ethyl iodoacetate with P. Freundler, a good friend of J.-A. Le Bel and obtained her postgraduate degree in 1932 at the Faculté des Sciences of the University of Paris. She then worked with Marc Tiffeneau at the Faculté de Médecine and, more independently, with Jeanne Lévy as a Director at the Fournier Institute, with a small team. Finally she passed her thesis on "The Contributions to the Study of the Ring Extensions: Nitrous Desamination of 1-Aminomethyl, 1-Cyclohexanols" in 1946. Appointed as Research Assistant at the CNRS, she soon played the role of a "Director" much before she was appointed to such a position in 1955. In 1961 when moved with her group to the Institut de Chimie des Substances Naturelles of Gif-sur-Yvette, she then became the Director of Research Group No. 12 of the CNRS Center of Thiais in 1968 and stayed in that position until her retirement 10 years later. In the 1970s she started working on nitrogen fixation by iron complexes in collaboration with A. E. Shilov and his group. After retiring, her scientific activity did not stop and she passionately continued working on reaction mechanisms until she passed away on April 24, 1990.

Blanka Tchoubar was an outstanding figure and a pioneer in the French chemistry of this century. For instance her work on the three-step transformation of cycloalkanone to higher homologues (1937) became a widely used classic, notably in the steroid series. Of very generous character she was an extremely rigorous mechanistic chemist and wrote two books on reaction mechanisms, the latter with André Loupy (1988). For more details, see the January 1992 issue of the *New Journal of Chemistry* on "Mechanisms and Processes in Molecular Chemistry", dedicated to her memory.



Didier Astruc obtained his "Thèse d'Etat" from the University of Rennes (1975) and did postdoctoral studies at MIT (1977). He was a CNRS Fellow in Rennes (1978–82) and has been a Professor of Chemistry at the University Bordeaux I since 1983 (except a sabbatical year in Berkeley, 1990–91). His interests are in electron-transfer mechanisms and processes, organometallic materials, and catalysis.

involved in the second part. Fast physical techniques such as time-resolved photoacoustic calorimetry and picosecond absorption spectroscopy have been recently helpful in understanding the microdynamics of ion-pair reactions. On the synthetic side many applications of the special salt effect are already known. They range from simple organic reaction to sophisticated photochemical devices, and the area is considerably growing. The synthetic chemists should find a powerful tool to control reaction pathways there.

## B. Specific Trends of Salt Effects Resulting from Exchange between Two Ion Pairs

It is probable that every reaction between two charged species, one negatively ( $A^-$ ) and the other positively ( $B^+$ ) must proceed via a transitory contact ion pair (CIP) containing both species ( $A^-B^+$ ):



where TS = transition state.

It is obvious that the rate of such a reaction must depend on the concentration of the intermediate ion pair.

$$v = k[A^-B^+] \quad (\text{eq 2})$$

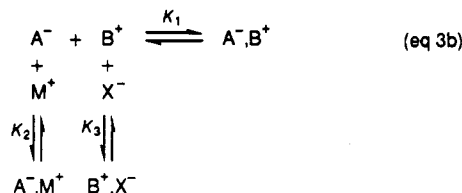
It follows that any factor disfavoring the formation of the latter must necessarily slow down the overall reaction:  $v$  decreases as  $[A^-B^+]$  decreases. Thus it must be disfavored by solvents with a large dielectric constant and by solvents susceptible to transforming the contact ion pairs (CIP) into solvent-separated ion pairs (SSIP).



When the contact ion pairs (CIP) and the solvent-separated ion pairs (SSIP) are in equilibrium, the position of the latter depends not only on temperature ( $K$  increases when  $T$  decreases) but also on the nature of the ions and of the solvent.<sup>1-7</sup>

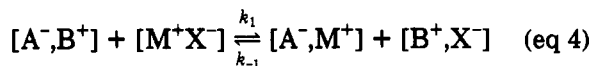
Another factor which can cause the slowing down and even the complete inhibition of this type of reactions

is the presence of a chemically inert salt ( $M^+X^-$ ) in the reaction medium. Indeed the equilibrium leading to the ion pairs in which the reaction takes place ( $K_1$ ) can be in competition with two other equilibria ( $K_2$  and  $K_3$ ) in the presence of a salt, resulting from ionic associations of the ions  $A^-$  and  $B^+$  with those of the added salt.



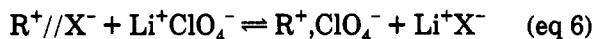
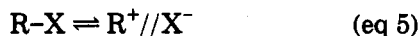
If the side ion pairs  $[A^{\cdot-}, M^+]$  and  $[B^{\cdot+}, X^-]$  are thermodynamically more stable than  $[A^{\cdot-}, B^{\cdot+}]$  or if the added salt is in large excess with respect to the reacting species, the reaction between the ions of the pair  $[A^{\cdot-}, B^{\cdot+}]$  is disfavored.

In nondissociating solvents ( $\epsilon < 10$ ) in which ions are essentially associated with their counterions,<sup>1-3</sup> the reaction occurring in a contact ion pair CIP ( $A^{\cdot-} B^{\cdot+}$ ) can be blocked by an added salt because of ion exchange between the two ion pairs.



$$K_E = k_1/k_{-1}$$

The fact that direct ion exchange among the two ion pairs can occur without prior dissociation into the free ions was evoked for the first time by Winstein.<sup>8</sup> On the basis of studies of the effect of added  $\text{LiClO}_4$  on the rate of solvolysis of alkyl arenesulfonates, Winstein concluded that the salt accelerated the rate by undergoing an ion-pair exchange with the solvent-separated ion pair generated by heterolysis of the sulfonate.  $[X^- = \text{ArSO}_3^-]$ .



Such an exchange prevents the initially formed solvent-separated ion pair from returning to the sulfonate precursor ("special salt effect"). Although Winstein concluded that the exchange reaction involved the solvent-separated ion pair, ion-pair exchange could occur in principle with either the contact or solvent-separated form.<sup>2,6,7,9</sup> One would expect that the mechanism of exchange, as well as the rate of exchange, would depend not only on the type of ion pairs involved but also on the specific interaction existing between the ions and the surrounding solvent molecules.

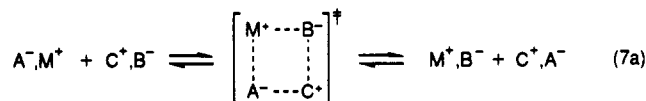
At the present time, such a process has received substantial support on the basis of various spectrometric measurements<sup>2,9-13,17,18</sup> allowing the determinations of equilibrium constants  $K_E$  and of rate constants  $k_1$ , for series of reactions based on eq 2.

Picosecond and nanosecond studies by absorption spectroscopy of the photoreduction of benzophenone by amines have been extensively envisaged.<sup>6,7,13</sup> They have been used to examine the thermodynamics of the ion-pair exchange between alkaline salts and ion-pair intermediates in these reactions (for a discussion, see

section III.B.1 dealing with photophysical studies). It was so concluded that the nature (SSIP or CIP) of ion pairs involved as well as their interaction with the solvent are of prime importance.

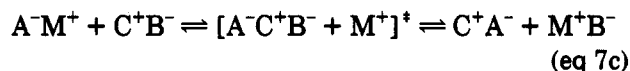
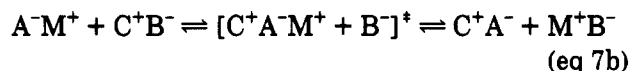
Several authors have addressed the problem of the intimate exchange mechanism between the two ion pairs, for example, the question of the structure of the transition state of such a bimolecular process.

Crampton and Grunwald have proposed that, in the transition state, the two ion pairs form a quadruplet (quadrupole) in which each ion is bound to two ions of opposite charge:<sup>2,9</sup>



In such a transition state, the bonds are lengthened with respect to those in each initial ion pair. This elongation requires all the more energy since the starting ion pair is more stable (tighter). This hypothesis was also considered later by other authors.<sup>2,10</sup>

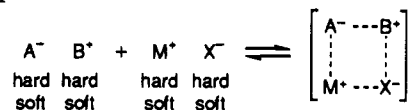
However, several studies have shown that, at least in some cases, the transition state is not a quadruplet but a triple ion:<sup>2,11,12,17,18</sup>



It is probable that both mechanisms of eqs 7a and 7b (or 7c) can compete.<sup>10</sup> It seems that the ion-pair exchange via a quadrupolar transition state (eq 3) dominates every time its formation is not sterically hindered.<sup>10</sup> In the opposite situation, the ion-pair exchange would preferentially proceed through a triplet in the transition state.<sup>10,17</sup>

The relative importance of these two mechanisms can also depend on the affinities of the ions for each other and especially of their relatively hard and soft characters. The symbiotic effect introduced by Pearson<sup>20</sup> states that hard acids (cations) prefer to coordinate to hard bases (anions) and that soft acids prefer to coordinate to soft bases. Particularly, four-centered mechanisms via quadrupoles could be favored when all the concerned ions are either hard or soft ones. This is noticeably the case when the ion pairs concerned are of the same type (SSIP or CIP), a favorable case according to Simon and Peters<sup>7</sup> (Scheme 1).

SCHEME 1

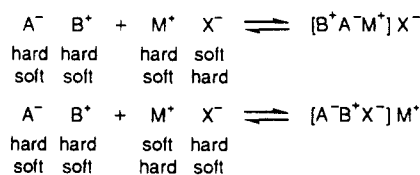


On the other hand, if one ion of different hardness is involved, a triple ion can be favored in connection with specific symbiotic interactions (Scheme 2).

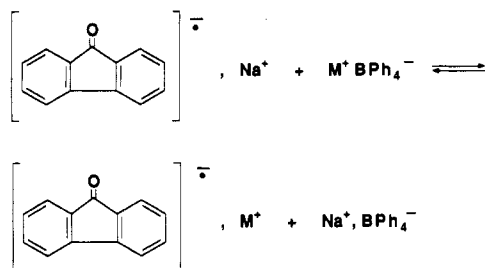
Thus ESR studies have shown that the exchange between ion pairs containing large anions proceeds via a triplet, as in Scheme 3 where both the fluorenyl and tetraphenylborate anions are large.

On the contrary, the exchange of sodium ketyls (where the ketyl anions are derived from fluorene or xanthone)

## SCHEME 2



## SCHEME 3



with NaI proceeds via a quadrupole ion in the transition state<sup>2,10,11,16</sup> (the iodide anion is now much smaller than BPh<sub>4</sub><sup>-</sup>).

The exchange of ions between solvent-separated ion pairs has been shown on several occasions. However its mechanism is not yet known.<sup>6,13,19</sup>



The photophysics of ion pairing of  $\beta$ -naphtholates in weakly and medium polar solvents was studied. It was shown that the broad absorption and emission bands of the  $\beta$ -naphtholate anion consist of overlapping spectra of CIP and SSIP types of ion pairs. The lifetime measurements show that an increasing cation radius favors the SSIP over the CIP. This is not a general observation since, for carbanions, the opposite tendency is usually reported.<sup>26,27,151,152</sup> The effect of adding salts on the spectra and lifetimes of  $\beta$ -naphtholates has been evaluated.<sup>17,18</sup> Additions of NaClO<sub>4</sub> transform the main part of the excited CIP sodium-naphtholate ion pair into SSIP as traced by the observed lifetime.

Thus if the reaction whose site is a CIP is effected in a nondissociating solvent having a small donor number (DN) and acceptor number (AN), the addition of a salt (M<sup>+</sup>X<sup>-</sup>) can inhibit the reaction of eq 9.



However, such a salt can only have an effect if the rate of the reaction  $v = k[\text{A}^- \text{B}^+]$  is lower than that of the ion exchange between the two ion pairs:  $v_E = k_E[\text{A}^- \text{B}^+][\text{M}^+ \text{X}^-]$ . If the concentration of added salt is much larger than that of the ion pair which is the reaction site ( $[\text{M}^+ \text{X}^-] \gg [\text{A}^- \text{B}^+]$ ), the ion exchange reaction becomes a pseudo-first-order process:

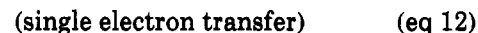
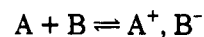
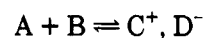
$$v_E = k'_E[\text{A}^- \text{B}^+] \text{ with } k'_E = k_E[\text{M}^+ \text{X}^-] \quad (\text{eq } 10)$$

It follows that the negative salt effect on the reaction 9 can operate only when  $k[\text{A}^- \text{B}^+] < k'_E[\text{A}^- \text{B}^+]$ , e.g.  $k < k_E[\text{M}^+ \text{X}^-]$ . For this reason, the inhibition of some reactions of the type of eq 9 whose rate constant  $k$  is very large requires a large excess of added salt M<sup>+</sup>X<sup>-</sup>.

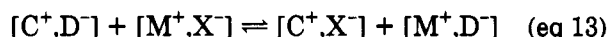
with respect to A<sup>-</sup>B<sup>+</sup>. This is sometimes the case for reactions between neutral species leading to charged species.

The formation of CIP is an important intermediate step in numerous reactions of various nature. The course of these reactions is deeply modified by addition of salts in the reaction media because of ion exchange between ion pairs. The present review illustrates this aspect of the salt effects whose interest is growing.

The ion pair C<sup>+</sup>D<sup>-</sup> (or A<sup>+</sup>B<sup>-</sup>, etc.), originating from a reaction between neutral products, can give rise to two classes of reactions: those resulting from the interaction between an electrophile and a nucleophile (in inorganic terms, inner-sphere transfer of an electron pair) and those arising from outer-sphere single electron transfer (SET) in which radicals are necessarily involved.

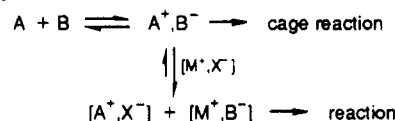


The reactions need also be classified according to their ergonicity. The nucleophile/electrophile reactions are often equilibrated, especially in organic chemistry; a major influence of the added salt M<sup>+</sup>X<sup>-</sup> is to dislocate the formed ion pair by double ion exchange. The rate of the inverse reaction ( $v_{-1}$ ) which depends on the concentration of the ion pair C<sup>+</sup>D<sup>-</sup> ( $v_{-1} = k_{-1}[\text{C}^+, \text{D}^-]$ ) is decreased and the ion-pair exchange is displaced to the right:



On the other hand, SET reactions can be strongly exergonic, equilibrated (close to isoergonicity), or endergonic. In an exergonic SET process, the salt has no influence on the SET which is fast and irreversible, but since it dislocates the ion pair formed, it inhibits the cage reaction (Scheme 4). Inorganic and organo-

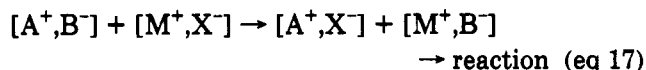
## SCHEME 4



metallic reactions belong to this category because of the large range of oxidation states and of redox potentials of the transition metal complexes.

In iso- and endergonic SET, the added salt displaces the ET equilibrium to the right by inhibiting the back ET, a situation similar to the nucleophile/electrophile reactions. If the endergonicity is weak, this salt effect can even be catalytic when the appropriate salt is chosen. If the endergonicity is large, a larger quantity of salt can be used to drive the ET; this is possible because the rate of double ion exchange among the ion pairs is very high, close to the diffusion-control limit. This case applies in particular to the salt effect in light-

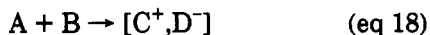
induced reactions:



A feature common to these categories is the possible occurrence of several pathways leading to several reaction products. The addition of a salt strongly influences this distribution through the dislocation of reactive ion pairs.

## II. Reactions between Nucleophiles and Electrophiles

In this part, we distinguish the reactions between neutral species and those between ionic species. In the first category, the charged species are created in a primary reaction according to



If the dielectric constant of the solvent is weak ( $\epsilon \leq 10$ ), only the CIP forms. The added salt also forms another CIP subsequent to dissolution and fast exchange between the ions of the two CIP's influences the chemistry, for instance by inhibiting the cage reaction within the CIP  $[C^+, D^-]$ . The many organic examples illustrating this situation have been gathered in the first section. In several instances, the solvent may be dissociating the CIP's into SSIP's and the mechanism of ion-pair exchange is uncertain, but these cases will be included as well in this first section since they are also organic.

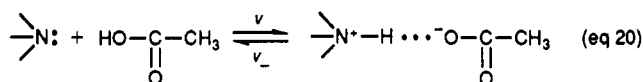
However they are somehow related to the second type of situation treated in the second section where the reactions are started with ionic species (organometallic examples). The ionic species introduced may form CIP's and/or SSIP's, depending on their nature and that of the solvent.



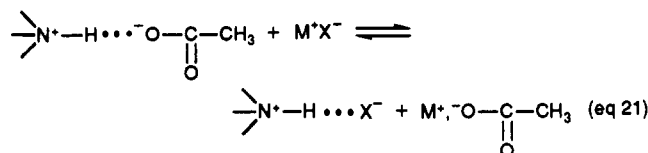
### A. Organic Reactions between Neutral Nucleophiles and Electrophiles

#### 1. Acidic-Basic Equilibria

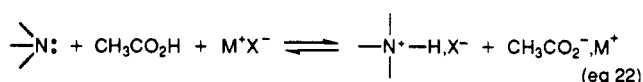
*a. Protonation of Amines by Acetic Acid.* It was shown, using alkaline colored indicators, that the protonation equilibrium (eq 20) of an amine by  $\text{CH}_3\text{CO}_2\text{H}$  is strongly shifted toward the protonated species by addition of a salt  $\text{Na}^+, \text{X}^-$  or  $\text{R}_4\text{N}^+, \text{X}^-$  ( $\text{X}^- = \text{Cl}^-, \text{I}^-, \text{ClO}_4^-$ ) and that this effect is all the more marked as the salt concentration is higher.<sup>21,22</sup> The shift to the right in eq 20 is essentially due to the slowing down of



the reverse reaction ( $v_-$ ) subsequent to the exchange between ion pairs shown in eq 21 (also when the acetate anion is associated to an alkali cation  $\text{Li}^+$  or  $\text{Na}^+$ , its ability to abstract a proton is greatly reduced<sup>24</sup>). As

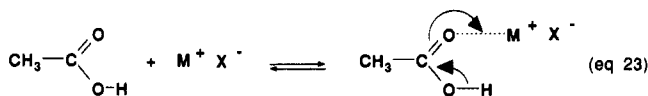


suggested by Bessière,<sup>21</sup> it is adequate to envisage the global equilibrium of eq 22 in the presence of a salt, rather than the equilibria of eqs 20 and 21 taken separately. Given the equilibrium shift rule, it follows

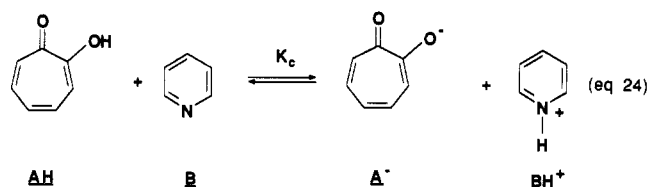


that the percentage of protonated amine should increase as the concentration of added salt increases, which has been confirmed by the experiment.<sup>21</sup>

Corriu et al. have indicated however that the shift of eq 20 toward the protonated species can also result from an enhancement of the proton-donor character of acetic acid upon interaction with the cation  $\text{M}^+$ , at least when the latter is  $\text{Li}^+$  or  $\text{Na}^+$  (eq 23).<sup>22,23</sup>



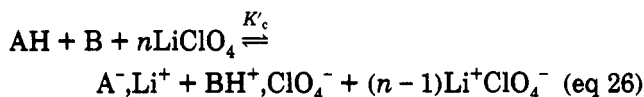
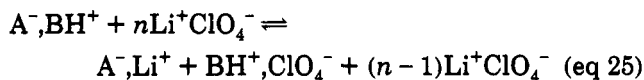
*b. Deprotonation of Weak Acids by Aromatic Amines.* Another apparently closely related salt effect is the dramatic influence of  $\text{LiClO}_4$  in ether solutions on deprotonation equilibria of weak acids such as phenols or tropolone by anilines or pyridines<sup>28</sup> (eq 24).



Pocker and Ciula have thoroughly studied this phenomenon in the case of eq 24.<sup>28</sup> Using UV measurements of the ratio  $[\text{A}^-]/[\text{AH}]$  in the presence of various  $\text{LiClO}_4$  concentrations, these authors have shown that the apparent equilibrium constant  $K_c$  of equilibrium 24 increases very drastically with the salt concentration: from  $1.9 \times 10^{-3}$  for  $[\text{LiClO}_4] = 4.8 \times 10^{-3} \text{ M}$  to 23.8 for  $[\text{LiClO}_4] = 2.95 \text{ M}$ . Thus  $K_c$  is multiplied by 12 500 when the  $\text{LiClO}_4$  concentration is 600 times higher.

Since all the measurements were taken in the presence of a high  $\text{LiClO}_4$  excess with respect to the reacting species (the molar ratio  $[\text{LiClO}_4]/[\text{AH}]$  varies from 80 to 49 000), the exchange equilibrium between two ion pairs must be totally shifted to the right in all the examined cases (eq 25).

Under these conditions, it follows that the actual equilibrium is as in eq 26. The fact that  $K'_c$  increases

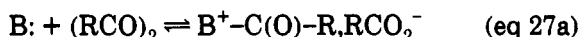


with the number of moles  $n$  of  $LiClO_4$  means that the ion pairs  $A^-, Li^+$  and  $BH^+, ClO_4^-$  are not free but associated with the salt in mixed aggregates when the  $LiClO_4$  excess is large. This aggregation stabilizes the ion pairs and thus decreases their mutual reactivity. One may consider that these ion pairs are solvated by  $LiClO_4$  and that their respective activity coefficients  $\gamma$  are consequently diminished. The consequence is that the equilibrium of eq 24 is shifted to the right. This shift is all the more marked as the number of  $LiClO_4$  molecules in the aggregate is larger. Experimentally this appears by the increase of the  $[A^-]/[AH]$  ratio as a function of  $LiClO_4$ , e.g. in the increase of  $K_c$  in eq 24.

Finally, Pocker and Buchholz<sup>28b</sup> showed that the ether solutions of  $LiClO_4$  contain two species in equilibrium in which  $Li^+$  is associated to one or two ether molecules:  $Li(Et_2O)^+, ClO_4^-$  and  $Li(Et_2O)_2^+, ClO_4^-$ . These are the species which are able to form mixed aggregates with other ions in the medium.<sup>27,28</sup> Note that the stabilization of ion pairs by aggregation with  $LiClO_4$  in ether is a general phenomenon. For instance, it causes the apparent equilibrium constant of  $Ph_3CCl$  to be  $7 \times 10^9$  higher in the presence of 5.05 M  $LiClO_4$  than in the absence of the salt.<sup>28b</sup>

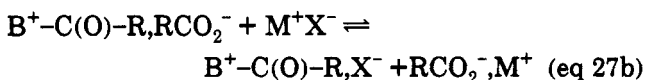
## 2. Acylation Equilibria of Neutral Molecules

The acylation equilibrium of eq 27a is the major process in condensation reactions between two nucleophiles in which acetic acid is involved. In this way, it



is possible to transform, by acylation, a nucleophilic substrate (B:) bearing an electron pair (pyridine, amine oxide, sulfoxide, pyrone, etc.) into a cationic intermediate  $[B^+ - C(O)R]$  susceptible of reacting with another nucleophilic substrate.

The reversibility of these reactions (eq 27a) is dramatically decreased in the presence of salts and in particular alkali perchlorates (eq 27b). The alkali salts



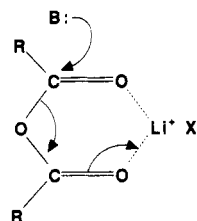
play a double role here:

(i) They slow down the inverse reaction subsequent to the exchange between two ion pairs (eq 27b). The equilibrium is notably shifted to the right because of the strong ionic association between two hard ions in the species  $RCO_2^-Li^+$  when the salt used is  $LiClO_4$ .

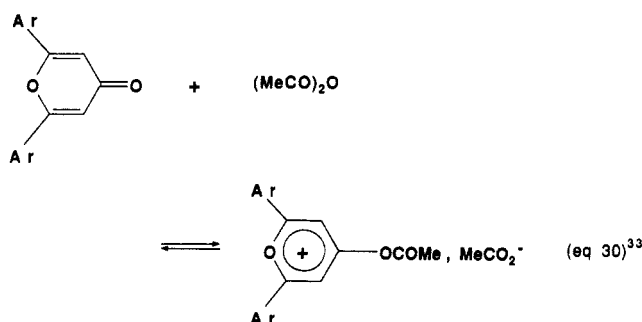
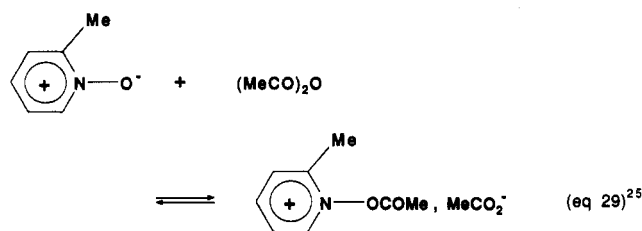
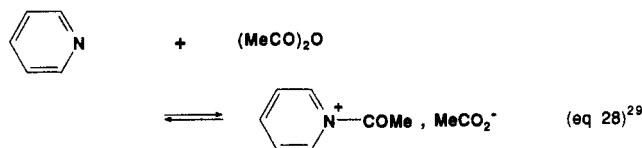
(ii) They accelerate the forward reaction by electrophilic catalysis by the cation of the added salt (Chart 1).

Quantitative and semiquantitative measurements of the shift magnitude of the equilibria as a function of the added salt concentration have been taken using

CHART 1



UV spectroscopy for the three reactions of eqs 28–30.



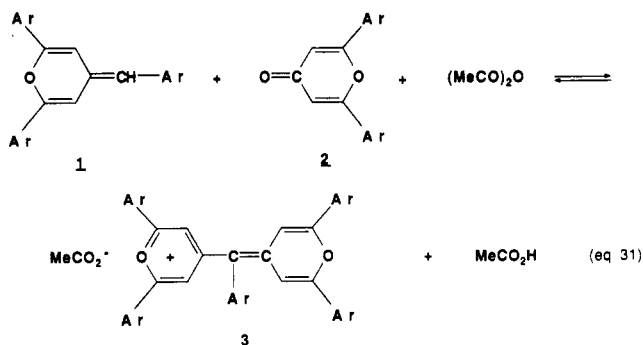
In the presence of a high  $NaClO_4$  concentration, these three equilibria are totally shifted toward charged species. For instance, in the pyridine cases (eq 28), the rate constant of the forward reaction is  $136 \text{ M}^{-1} \text{ s}^{-1}$  in the presence of 4 M  $NaClO_4$  and  $190 \text{ M}^{-1} \text{ s}^{-1}$  with 6 M  $NaClO_4$ .<sup>29</sup>

For equation 30, the UV and NMR spectroscopies interestingly show that  $\gamma$ -pyrone only gives traces of pyrylium salts in pure acetic anhydride, but a complete transformation is obtained in the presence of excess  $LiClO_4$ . When a solvent solvating the inorganic cation is added to this reaction medium (for instance DMF), the equilibrium is shifted toward the pyrone formation. These results unambiguously show that, in a weakly dissociating medium (a mixture of chloroform and acetic anhydride), the salt provokes the trapping of  $CH_3CO_2^-$  by  $Li^+$  subsequent to double ion-pair exchange (eq 27b). Let us emphasize that this salt effect on the position of the acylation equilibrium of the  $\gamma$ -pyrone (eq 30) has deep consequences for the reaction of eq 31 where condensation of a methylenepyrans 1 with the  $\gamma$ -pyrone 2 leads to the corresponding cyanine 3 upon the action of acetic acid.<sup>30–33</sup>

The yield of this reaction increases from a few percent in the absence of salt to 85–90% in the presence of a large  $NaClO_4$  excess. In addition, the reaction is strongly accelerated by salts whose efficiencies vary as follows:<sup>33</sup>



The first reaction stage is the formation of the pyrylium

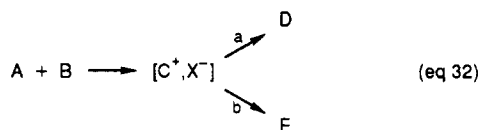


cation by reversible acylation of the  $\gamma$ -pyrone. The acceleration of the reaction by salts is due to the shift of the preequilibrium toward the pyrylium cation subsequent to the exchange between two ion pairs (vide supra) whose concentration determines the global reaction rate. The improvement of the latter can also be attributed to the exchange reaction between two ion pairs, one of which is formed by the reaction product 3 and the other by the added salt  $\text{Na}^+\text{ClO}_4^-$ . Indeed this reaction is reversible, due to the instability of the cyanine salt 3 in the presence of its anion  $\text{MeCO}_2^-$ . When the latter is replaced by  $\text{ClO}_4^-$ , the reaction is no longer reversible, the cyanine being stable as a perchlorate salt.<sup>31</sup>

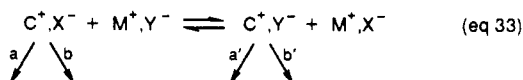
A salt effect, favorable to the yield as well as to the reaction rate, has also been found in the condensation reaction of methylenepyran with *p*-nitrosodimethylaniline.<sup>34</sup>

### 3. Salt Effects on the Product Distribution in Reactions Occurring in Ion Pairs

If a reaction involving the intermediate formation of an ion pair further leads to different paths, a mixture of products is necessarily obtained (eq 32). The

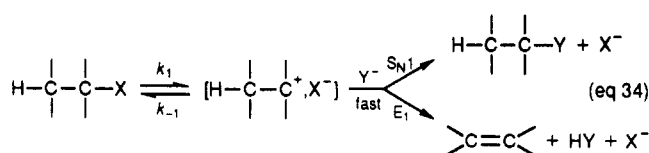


proportion of the product yields depends on the ratio of the reaction rates of the two competitive reaction paths a and b. Thus any factor influencing the latter will affect the D/E ratio. On the other hand, it is well known that the reaction rates markedly depend on the ion-pair structures. This phenomenon often involves mechanistic changes in the reactions of these ion pairs. Large variations of product distributions may result. It is also conceivable that the presence of a salt might influence the product distribution of the reaction by partially or totally dislocating the intermediate ion pair formed. This effect can then be attributed to the exchange reaction between two ion pairs giving rise to new species (eq 33). A series of examples will now be

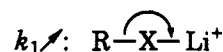


shown to illustrate this phenomenon and emphasize its general character.

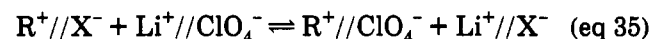
#### a. $E_1/S_N1$ Competition.



Upon addition of alkaline salts, the ionization of the substrates  $\text{RX}$  (eq 34) is notably accelerated, especially under the influence of lithium salts. According to the interpretation proposed by Winstein,<sup>8</sup> this effect is attributable on one hand to the acceleration of the ionization step by the "normal salt effect"

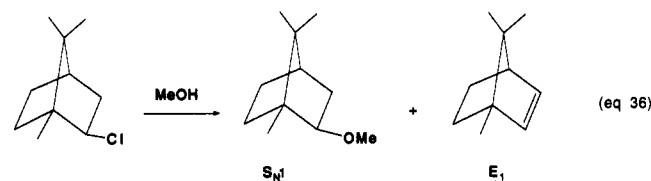


but on the other hand to the "special salt effect" which is the consequence of an exchange reaction (eq 35) between two ion pairs and disfavors the ion recombination ( $k_{-1} \searrow$ ). In addition, the carbocation ( $\text{R}^+$ )



reactivity is different depending on whether it is engaged in an ion pair with  $\text{X}^-$  or with  $\text{ClO}_4^-$ , the latter being much less tightly bound than the former, thus more reactive. The ratio of the products  $E_1/S_N1$  can be modified by the effect of a salt differently influencing the two fast steps. The ion-pair structure causing the reaction as well as the relative H- and C-nucleophilicities of  $\text{Y}^-$  are modified by the presence of the salt.

Studying the solvolysis of isobornyl chloride (eq 36), Bunton et al.<sup>35</sup> observed opposite salt effects with alkaline chlorides (increase of the olefin %) and with the corresponding perchlorates (increase of the ether %)



Opposite effects of the addition of  $\text{LiClO}_4$  were observed in the acetolysis depending on the nature of the substrates:

(i) With cyclohexyl tosylate, in the presence of a buffer ( $\text{MeCO}_2\text{K}$ ), the  $S_N1/E_1$  ratio varies from 10/90 in the absence of a salt to 45/55 in the presence of  $\text{LiClO}_4$ , thus provoking a marked decrease of the elimination product formation.<sup>36</sup>

(ii) With 4-*tert*-butylcyclohexyl 2,4-dinitrobenzenesulfinyl, the addition of the same salt induces an increase in the proportion of olefin from 22 to 48% in the presence of 1 equiv of  $\text{LiClO}_4$ .<sup>37</sup>

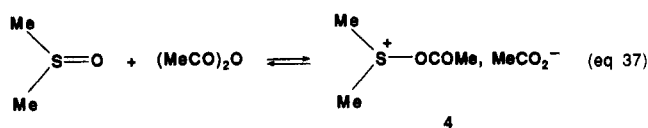
In a number of examples where the global reaction rate is increased by the addition of a salt, the product ratio  $S_N1/E_1$  is unchanged.<sup>38,39</sup> The two antagonistic phenomena, modifying on one hand the reactivity of the cation  $\text{R}^+$  and on the other hand that of the nucleophile  $\text{Y}^-$ , then compensate each other.

b. *Reactions of "Activated Sulfoxides"*. With anhydrides, the sulfoxides, in particular DMSO, give an equilibrated reaction leading to (acyloxy)sulfonium salts<sup>40,41</sup> (eq 37). Salt 4 is only stable at low temper-

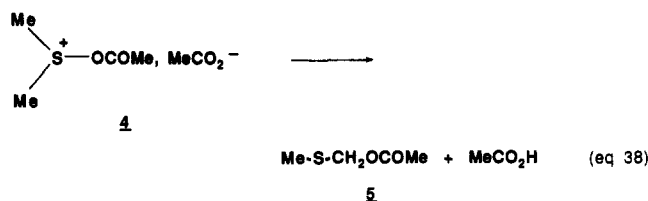


Table 1

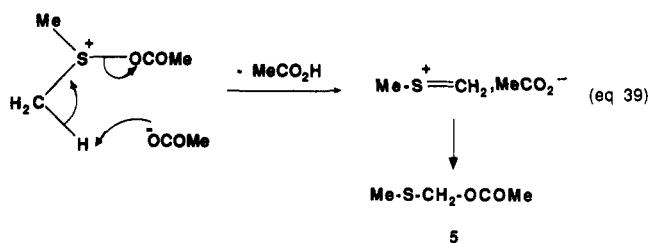
salt (1.5 M)	% E <sub>1</sub>
—	42
LiCl	46
NEt <sub>4</sub> Cl	58
LiClO <sub>4</sub>	36
NaClO <sub>4</sub>	33



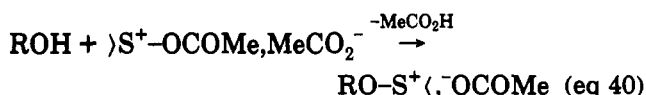
ature.<sup>40</sup> At 20 °C, the ion pair 4 reacts to give the acetoxy sulfurane 5 (eq 38).



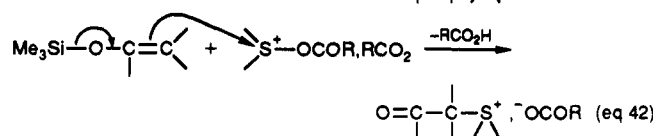
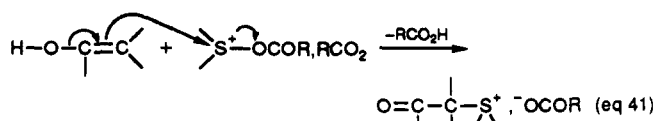
The mechanism of this reaction, discovered very long ago by Pummerer<sup>42</sup> has been subjected to multiple studies.<sup>43</sup> It can be schematized according to eq 39; the elimination probably occurs by a two-step process with the formation of an ylide intermediate CH<sub>2</sub>=S<sup>+</sup>(Me)-OCOMe.



It is known that (acyloxy)sulfonium salts such as 4 react with a whole series of nucleophiles to give substitution reactions of the sulfur atom<sup>40</sup> (see for instance eq 40). They also react with electron-rich



carbon-carbon double bonds such as enols<sup>4</sup> or enoxysilanes<sup>45</sup> or even with α-disubstituted hydrocarbons<sup>46</sup> (eqs 41 and 42).



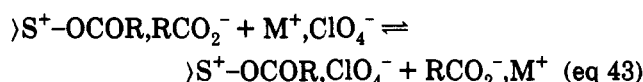
The yields of these reactions are often quite low because they always compete with Pummerer's reaction. Since the latter occurs in a contact ion pair, it can be foreseen that it would be slowed down or totally

Table 2. PhCOCH<sub>2</sub>COMe/DMSO/Ac<sub>2</sub>O (1:1:2.5) with a Reaction Time of 0.5 h

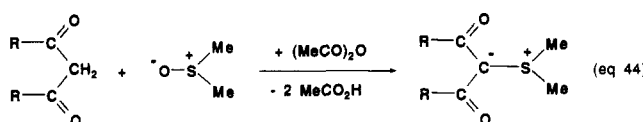
molar ratio, salt/DMSO	yield %
—	0 <sup>a</sup>
LiClO <sub>4</sub> , 1:1	64
NaClO <sub>4</sub> , 1:1	50

<sup>a</sup> 40% after 20 h.

inhibited in the presence of a salt whose anion is not basic (for instance ClO<sub>4</sub><sup>−</sup>) because of the double ion pair exchange of eq 43. The direct consequence of such



a special salt effect would be a significant increase of the reaction yields. To our knowledge, there is only one reported example of the study of salt effects on reactions involving an (acyloxy)sulfonium salt. It concerns the condensation of DMSO with β-dicarbonyl compounds in acetic anhydride at 100 °C, leading to stable sulfonium ylides<sup>47</sup> (eq 44).



Strzelecka<sup>48</sup> showed that, in the presence of 1 equiv of NaClO<sub>4</sub> or LiClO<sub>4</sub>, this reaction is accelerated 40-fold, and that its yield is considerably increased (Table 2).

In order to interpret this double salt effect, it is appropriate to refer to the mechanism of this reaction. Its first step is the nucleophilic attack of the acyloxysulfonium cation by the enol of β-diketone (Scheme 5). Recall that the β-diketones are essentially present in solution in their enolic form, about 80%; the latter is stabilized by an intramolecular hydrogen bond. The resulting compound 6 is a strong acid;<sup>44</sup> it undergoes a spontaneous deprotonation under the influence of the solvent (eq 45) whatever the associated anion (acetate or perchlorate); this leads to the stable ylide (Scheme 5).

The double salt effect observed must be due to the exchange reaction between the ion pairs (eq 43). This exchange:

(i) Provokes the shift of eq 37 toward the acyloxysulfonium and therefore the acceleration of the substitution reaction of Scheme 5.

(ii) Slows down the competitive Pummerer reaction (eq 38) by dislocating the ion pair 4 within which this reaction occurs and whose concentration determines its rate.

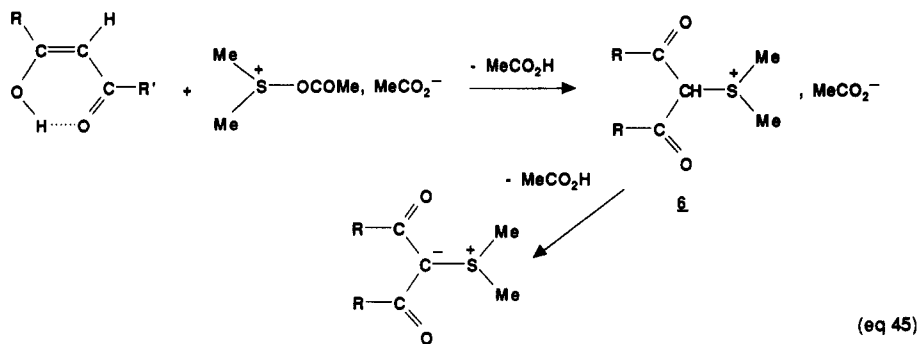
These results move in the direction of our above prediction concerning the beneficial effect of salts on substitution reactions whose site is an acyloxysulfonium cation.

c. *Opening of Epoxides in an Acidic Medium.* The epoxide opening reactions are considered as nucleophilic substitutions involving a weak leaving group<sup>49</sup> which therefore requires an electrophilic assistance to proceed.

In an acidic medium, the epoxides can give rise to two competing reactions subsequent to complexation

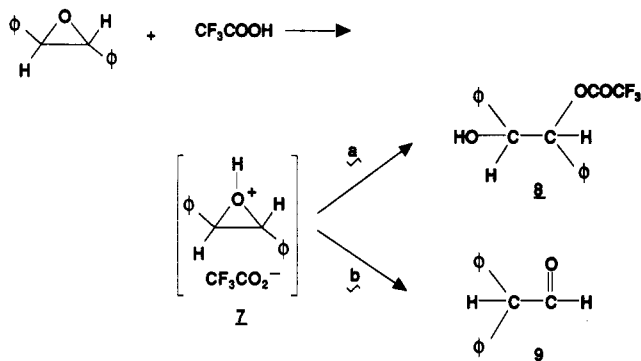


## SCHEME 5



between the proton (or a Lewis acid) and the oxygen atom (Scheme 6):

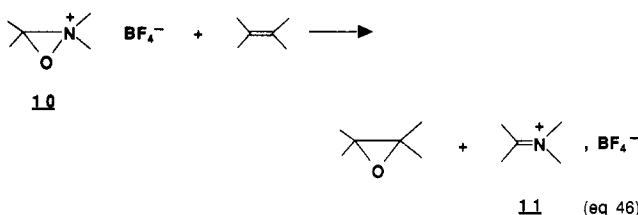
## SCHEME 6



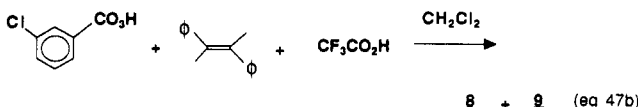
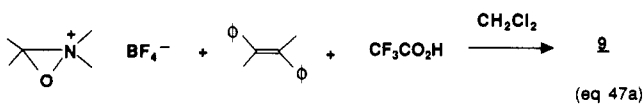
(i) Nucleophilic substitution a by the counteranion of the acid on the protonated epoxide.

(ii) Formation of the carbocation, then rearrangement b.

The oxaziridinium salts 10 are double bond epoxidizing reagents leading, along with epoxides, to immonium salts 11 (eq 46).

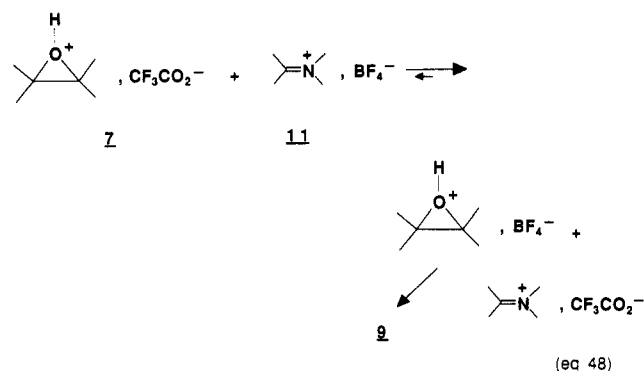


In the presence of 1 equiv of  $\text{CF}_3\text{CO}_2\text{H}$ , only the aldehyde 9 is obtained (Scheme 6) when the epoxide has been formed in situ from 10 (eq 47a). In contrast, an approximately equimolar amount of 8 and 9 are obtained when the epoxide is prepared in situ by reacting *m*-chloroperbenzoic acid with the same olefin (eq 47b).<sup>50</sup>



This difference in results can be attributed to the intervention of the immonium salt 11 generated during the epoxidation step, for reaction a. Subsequent to

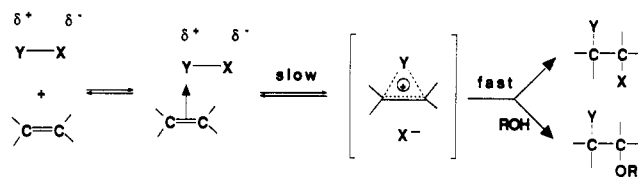
exchange between the two ion pairs 7 and 11, these salts can dislocate the ion pair 7 and therefore inhibit the formation of 8 (eq 48).



This result shows that by treating the epoxide in acidic medium, one can selectively obtain the rearrangement products when a salt whose anion is not nucleophilic is present in the reaction mixture. This effect then results from an exchange between two ion pairs.

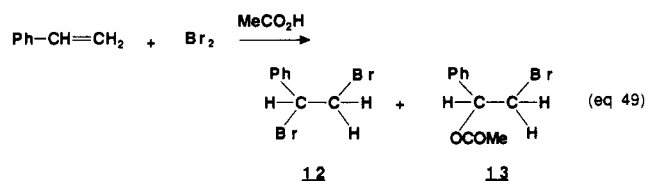
d. *Electrophilic Additions on Olefins.* Electrophilic addition reactions result from the attack of a carbon-carbon double bond by electrophilic reagents. During the slow step, a more or less symmetrical bridged cationic species is formed from a  $\pi$ -type complex. The subsequent evolution of these cations (Scheme 7) generates the reaction product(s) during the fast steps

## SCHEME 7



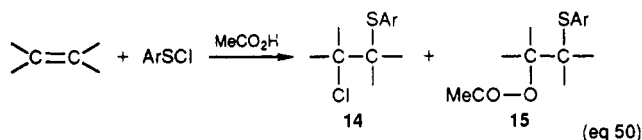
by combination with the counteranion or with another nucleophile (anion or solvent).

For example, the reaction of bromine with styrene in acetic acid gives a mixture of the dibrominated derivative 12 and brominated acetate 13 (eq 49).

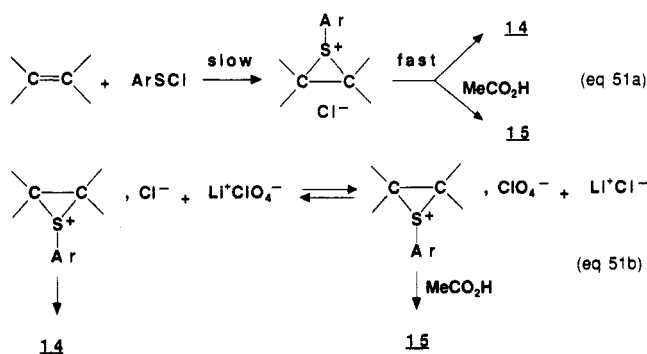


Rolston and Yates<sup>51</sup> have shown that the ratio of 13/12 is notably influenced by addition of lithium salts. This ratio is 0.5 in the absence of a salt; it decreases to 0.2 in the presence of 0.1 M LiBr and increases to 1 with 0.1 M LiClO<sub>4</sub>.

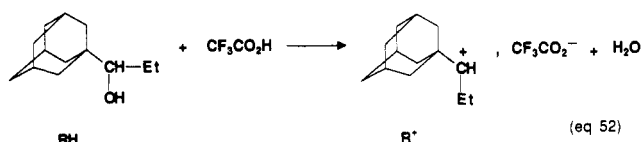
An analogous effect of LiClO<sub>4</sub> was observed in the reaction of arenesulfonyl chlorides ArSOCl on olefins in acetic acid<sup>52</sup> (eq 50).



The addition of LiClO<sub>4</sub> provokes a significant increase of the proportion of 15.<sup>52</sup> The latter is all the larger as the salt concentration is higher.<sup>53</sup> This result is in accordance with the hypothesis of an intermediate episulfonium cation<sup>52,54</sup> (eq 51a). The LiClO<sub>4</sub> effect on the mode of transformation of the intermediate cation is then attributable to the exchange reaction between two ion pairs<sup>55</sup> (eq 51b). The ratio 15/14 depends on the position of this equilibrium; it increases with the salt concentration.



*e. Aromatic Electrophilic Substitutions.* Kovalev et al.<sup>56</sup> have recently shown that aromatic compounds can be alkylated using secondary alcohols such as adamantylpropanol (eq 52) in a trifluoroacetic acid medium when the reactions are carried out in the presence of a catalytic amount of LiClO<sub>4</sub> (20% with respect to each of the reagents). In the first step, the alcohol in CF<sub>3</sub>CO<sub>2</sub>H gives the corresponding carbocation, engaged in an ion pair together with CF<sub>3</sub>CO<sub>2</sub><sup>-</sup>.



The beneficial effect of LiClO<sub>4</sub> is probably due to an exchange equilibrium of ion pairs with [CF<sub>3</sub>CO<sub>2</sub><sup>-</sup>, R<sup>+</sup>]. The latter then generates a new species [R<sup>+</sup>, ClO<sub>4</sub><sup>-</sup>]. By suppressing the internal ion recombination susceptible to giving the ester ROCOCF<sub>3</sub>, the electrophilic aromatic substitution process would therefore be favored (attack of the phenyl ring, eq 53).

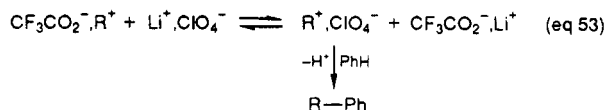


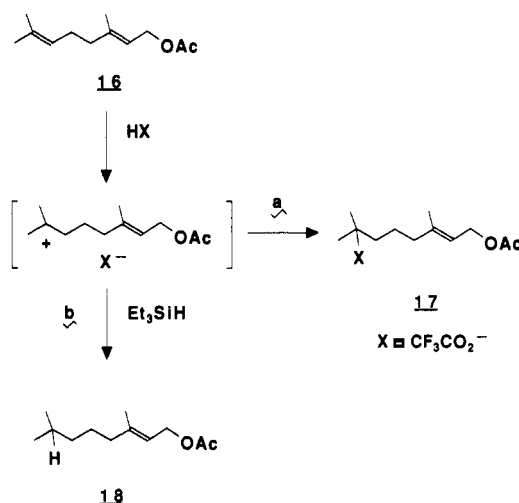
Table 3

conditions	salt	18/17
22 h, 50 °C	no salt	24/54
	0.1 equiv LiClO <sub>4</sub>	80/20
22 h, 20 °C	1 equiv LiClO <sub>4</sub>	90/10

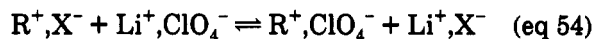
*f. Reductions by Silanes in Acidic Medium.* In the presence of an acid HX, the polyprenols 16 undergo an electrophilic addition of HX on the terminal double bond with the formation of a carbocation engaged in an ion pair with X<sup>-</sup>. When they are submitted to the system CF<sub>3</sub>CO<sub>2</sub>H (2.5 equiv)/Et<sub>3</sub>SiH (2 equiv), two competing reactions can occur<sup>57</sup> as follows:

(i) Addition of the acid onto the terminal double bond, leading to 17 (Scheme 8, path a) subsequent to a reaction proceeding within the intermediate ion pair formed.

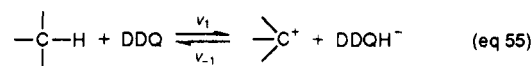
SCHEME 8



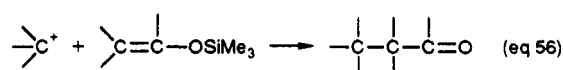
(ii) Reaction with the silane leading to the reduction product 18 (Scheme 8, path b). The reduction yield is remarkably improved in the presence of LiClO<sub>4</sub><sup>57</sup> (Table 3). The role of LiClO<sub>4</sub> can be attributed to a "special salt effect", i.e. the exchange of the ion pairs in eq 54 inhibiting the reaction between the carbocation and the anion X<sup>-</sup>.



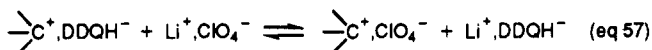
*g. Formation of Carbon-Carbon Bonds in Oxidizing Media.* Hayashi and Mukaiyama<sup>58</sup> have elaborated a new method of forming carbon-carbon bonds. This method consists in transforming a neutral molecule into a cationic species using a good oxidant such as 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) capable of hydride abstraction (eq 55). The cationic species



formed in this way then reacts with a silylated nucleophilic reagent having an ionic character, such as in eq 56. The reaction yield is improved from 23 to 82% in

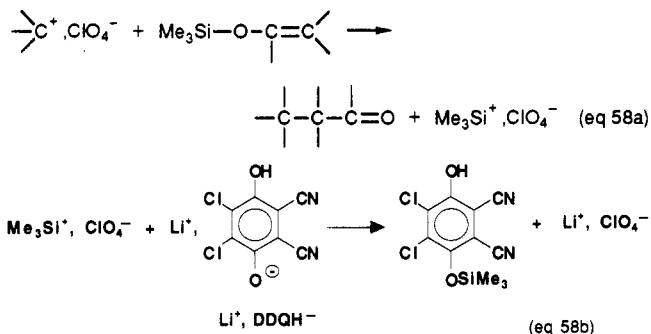


the presence of  $\text{LiClO}_4$  due to the exchange between the two ion pairs (eq 57). The inverse reaction of the



cation formation reaction in eq 55 is therefore inhibited ( $\nu_{-1} \searrow$ ).

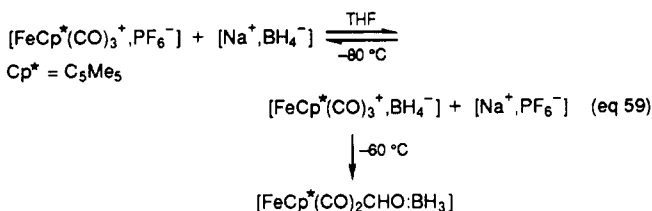
Note that  $\text{LiClO}_4$  is used in catalytic amount ( $\text{LiClO}_4/\text{substrate}$ , 0.1), being regenerated in the last reaction step of the mechanism (eq 58b).



## B. Organo-Transition Metal Reactions between Ionic Substrates

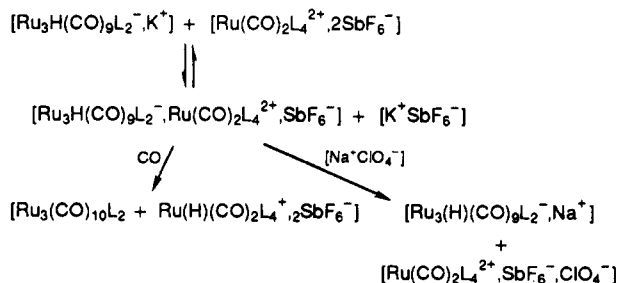
### 1. Reactions within the Ion Pair and Inhibition by Salts

There is ample evidence that double ion exchange between ion pairs is responsible for reactions between ionic species. In the iron-activated carbonyl reduction by  $\text{NaBH}_4$  in THF, neither of the starting materials is THF soluble, but a THF soluble species is detected by  $^1\text{H}$  NMR in THF- $d_3$  before the reaction, indicating that borohydride becomes the counteranion of the organoiron cation in a contact ion pair (CIP) at  $-80^\circ\text{C}$ .<sup>59</sup> Additional  $\text{NaPF}_6$  obviously displaces the ion-pair exchange equilibrium toward the counterproductive direction (eq 59). Similarly,  $\text{NaClO}_4$  inhibits the



hydride transfer between ionic ruthenium complexes<sup>60</sup> (Scheme 9).

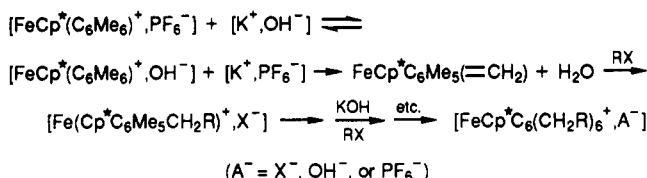
### SCHEME 9



In the reaction of  $\text{FeCp}(\text{C}_6\text{Me}_6)^+\text{PF}_6^-$  with  $\text{KOH}$  and a halide  $\text{RX}$  ( $\text{R}$  = alkyl, allyl, benzyl;  $\text{X}$  = Cl, Br, I), the first step is the deprotonation of a methyl group by

$\text{KOH}$ . This step is only feasible if double ion exchange produces naked, reactive  $\text{OH}^-$  as a counteranion of the organoiron cation, a mechanism reminiscent of phase-transfer catalysis.<sup>61</sup> The final hexaalkylated reaction products partly contain  $\text{OH}^-$  as counteranion. Attempts to perform the reaction in the presence of 1 equiv of  $\text{NaPF}_6$  did not work because again the double ion exchange equilibrium is displaced toward the wrong direction (Scheme 10).

### SCHEME 10

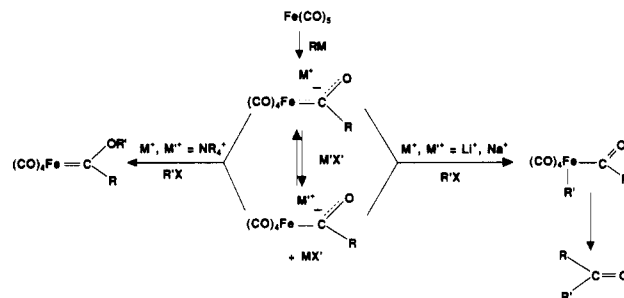


These simple examples illustrate the crucial role of ion pairs in the reactions between ionic species. Contrary to the favorable salt effect found in the reactions between neutral molecular species, the reactions between ions are subjected to an inhibiting salt effect. The major point here is that ionic species are brought together within an ion pair before reacting. In this way they are more reactive because they are no longer bound to their original counterion; on the other hand, their electrostatic interaction is now the driving force of the desired reaction.

### 2. Change in Rate and Selectivity by Variation of Counteranion

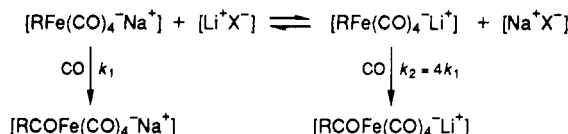
Double ion exchange could also orientate the selectivity of reactions. Although no salt effect has been reported in the alkylation of acylcarbonylmetalates, they can easily be anticipated after the studies by Semmelhack et al.<sup>62</sup> These authors reported that the regioselectivity of the alkylation depends on the nature of the counteranion, at least in the case of iron. Fischer et al. had shown that these anions are easily available from the reaction of carbanions on metal carbonyls.<sup>63</sup> As for enolates,<sup>64</sup> alkylation can occur on the hard site (oxygen) or on the soft one (metal). In the free anion (no coordination of the oxygen), the alkylation is under charge control and occurs on the oxygen atom.<sup>64</sup> On the other hand, with small metal cations in nondissociating solvents, the oxygen center is bound to the metal cation, acting as a Lewis acid in a contact ion pair (CIP); the reaction of the electrophile is then under orbital control and the metal is the reactive center. From these results, it is expected that a desired selectivity can be obtained by addition of a suitable salt which will provoke double ion exchange (Scheme 11).

### SCHEME 11



One may extend this concept to the reactivity of a large variety of anions which depends on their binding to the counteranion. Such is the case for Collman's migratory insertion of a carbonyl into the iron-alkyl bond of  $\text{RFe}(\text{CO})_4^-$ . This reaction is accelerated by the assistance of small alkaline metal counteranions (500 times faster with  $\text{Na}^+$  than with  $n\text{Bu}_4\text{N}^+$  for  $\text{R} = \text{alkyl}$ ). Double ion exchange induced by addition of an external  $\text{Li}^+$  salt will undoubtedly accelerate this reaction. It is known that the  $\text{Li}^+$  salt reacts 4 times faster than the  $\text{Na}^+$  one<sup>65</sup> (Scheme 12).

SCHEME 12



### III. Single Electron Transfer Reactions

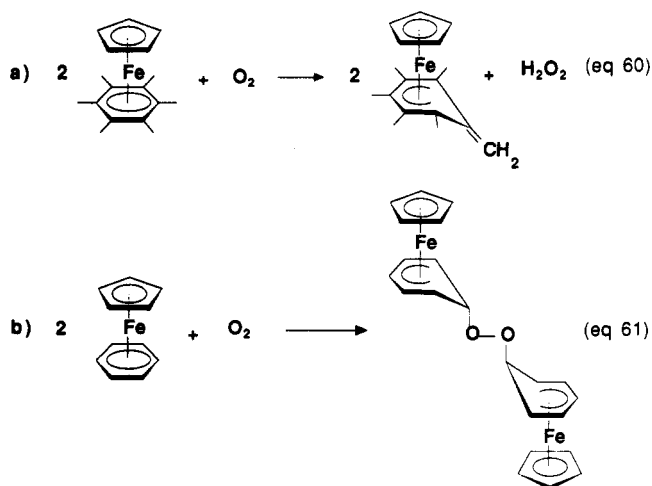
#### A. Organo-Transition Metal Ion Pairs Generated by SET from Neutral Donors and Acceptors

Organo-transition metal species are especially adequate for SET because of their great ability to change their redox states. The reactivity of the ion pairs formed by SET from a neutral organometallic species and a neutral acceptor is dramatically dependent on the presence of an added salt. However, one may distinguish at least two categories of situations depending on the ergonicity of the SET step.

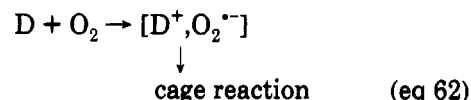
##### 1. Exergonic Generation of $\text{O}_2^{\cdot-}$ from $\text{O}_2$ and Organo- $\text{Fe}^{\text{I}}$ Electron Reservoir Complexes: Inhibition of the Cage Reaction of $\text{O}_2^{\cdot-}$ by $\text{Na}^+ \text{PF}_6^-$

The generation of  $\text{O}_2^{\cdot-}$  in solution, not easy with insoluble salts of  $\text{O}_2^{\cdot-}$  or requiring special media in electrochemistry,<sup>66</sup> can be simply carried out in common solvents using the soluble  $\text{Fe}^{\text{I}}$  sandwiches  $[\text{Fe}(\text{C}_5\text{R}_5)(\text{C}_6\text{R}'_6)]$  ( $\text{R} = \text{H}$  or  $\text{Me}$ ,  $\text{R}' = \text{H}$ ,  $\text{Me}$ , or  $\text{Et}$ ) and derivatives. The  $E^\circ$  value of the reversible system  $\text{O}_2/\text{O}_2^{\cdot-}$  is  $-0.7 \text{ V}$  vs SCE in pyridine.<sup>66,67</sup> Although it slightly depends on the solvent, it is much lower than the  $E^\circ$  value of all the reversible systems  $[\text{Fe}(\text{C}_5\text{R}_5)(\text{C}_6\text{R}'_6)]^{0/+}$  (e.g.  $E^\circ = 1.55 \text{ V}$  vs SCE for  $\text{R} = \text{H}$ ,  $\text{R}' = \text{Me}$ ).<sup>68</sup> The SET step is thermodynamically downhill and thus, according to the Marcus theory,<sup>69</sup> very fast.

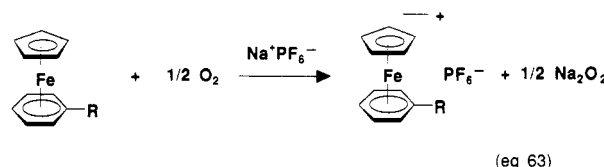
In the absence of a salt, the reaction of  $\text{O}_2$  with the  $\text{Fe}^{\text{I}}$  complexes either gives benzylic H atom abstraction (overall eq 60) or peroxide dimers (eq 61).<sup>70</sup>



In both cases, SET gives ion pairs  $[\text{D}^+, \text{O}_2^{\cdot-}]$  in which  $\text{O}_2^{\cdot-}$  either deprotonates  $\text{D}^+$  at the benzylic position (eq 61a) or gives nucleophilic addition onto the benzene ligand of  $\text{D}^+$  activated by the positively charged, 12e moiety  $(\text{FeC}_5\text{R}_5)^+$  (eq 61b). This mechanism is summarized in eq 62.

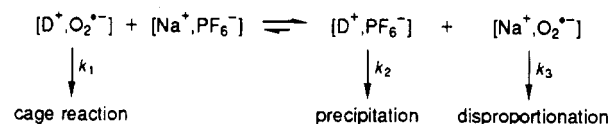


When the reactions are carried out in the presence of 1 equiv of  $\text{Na}^+ \text{PF}_6^-$ , the cage reaction products are not formed at all, and instead  $\text{D}^+ \text{PF}_6^-$  and  $\text{Na}_2\text{O}_2$  are obtained (eq 63).<sup>71</sup>

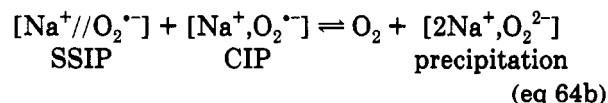


In the presence of  $\text{Na}^+ \text{PF}_6^-$ , the ion pair  $[\text{D}^+, \text{O}_2^{\cdot-}]$  can be metathesized and the equilibrium of (Scheme 13) is shifted to the right for both thermodynamic and kinetic reasons.

SCHEME 13



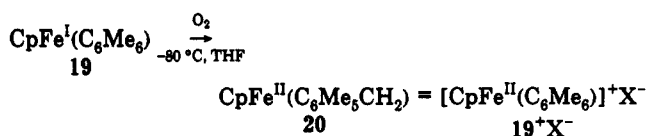
The thermodynamic of Scheme 13 is in favor of the disproportionation products because both small ions  $\text{Na}^+$  and  $\text{O}_2^{\cdot-}$  are together as well as both large ions  $\text{D}^+$  and  $\text{PF}_6^-$ . The kinetics of disproportionation of  $\text{O}_2^{\cdot-}$  is known to be extremely fast in the presence of protons or of transition metal ions. The disproportionation of  $\text{O}_2^{\cdot-}$  induced by  $\text{Na}^+$  can be accounted for in terms of the large difference of energy between the CIP and the SSIP. Indeed, the electrostatic attraction is very large between both small charged ions  $\text{Na}^+$  and  $\text{O}_2^{\cdot-}$  and is thus much larger in the CIP than in the SSIP (eq 64a). It is accordingly proposed that the more energetic SSIP reduces the CIP, a reaction eventually favored by the insolubility of sodium peroxide (equation 64b).



A further argument in favor of the salt effect on the reactivity of  $\text{O}_2$  with the  $\text{Fe}^{\text{I}}$  complexes is brought about by variations in the sizes of the cation and the anion in the added salt  $\text{M}^+ \text{X}^-$ . Such variations were carried out for both eqs 61a and 61b and gave analogous results consistent with the rationalization represented in Scheme 13 (Tables 4 and 5).

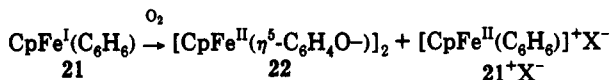
##### 2. Disproportionation of $\text{Fe}^{\text{I}}$ Complexes in the Presence of P Donors: Inhibition of Radical Pathways and Induction of SET by $\text{Na}^+ \text{PF}_6^-$ <sup>72,73</sup>

Extremely electron rich 19e  $\text{Fe}^{\text{I}}$  species can be generated upon displacement of the arene ligand by P

**Table 4. Salt Effect on the Reactivity of  $O_2^-$  as a Base in the Reaction**

M <sup>+</sup> X <sup>-</sup>	20 <sup>a</sup>	19 <sup>+</sup> X <sup>-a</sup>
without	92	8
n-Bu <sub>4</sub> N <sup>+</sup> PF <sub>6</sub> <sup>-</sup>	85	15
K <sup>+</sup> PF <sub>6</sub> <sup>-</sup>	45	55
K <sup>+</sup> PF <sub>6</sub> <sup>-</sup> = 18-crown-6	83	17
Na <sup>+</sup> PF <sub>6</sub> <sup>-</sup>	0	100
Na <sup>+</sup> BF <sub>4</sub> <sup>-</sup>	30	70
Na <sup>+</sup> F <sup>-</sup>	65	35

<sup>a</sup> Percent of 20 and 19<sup>+</sup>X<sup>-</sup> determined by weight (reactions are immediate). At 20 °C, the crude yields are 97 % for 20 and 3 % for 19; <sup>+</sup>PF<sub>6</sub><sup>-</sup>. Concentrations of both 19 and the salt in THF (30 mL) are 0.033 mol L<sup>-1</sup>. With other CpFe(arene) complexes (arene = toluene, mesitylene, pentamethylbenzene, ethylbenzene, fluorene), analogues of 20 are not formed in the presence of 1 equiv of Na<sup>+</sup>PF<sub>6</sub><sup>-</sup> under identical conditions 90–100 % yield of [CpFe(arene)<sup>+</sup>]PF<sub>6</sub><sup>-</sup>. Superoxide ion was characterized by its characteristic ESR spectra at 77 K in reaction of O<sub>2</sub> with 19 in frozen THF solution.

**Table 5. Salt Effect on the Reactivity of  $O_2^-$  as a Nucleophile in the Reaction**

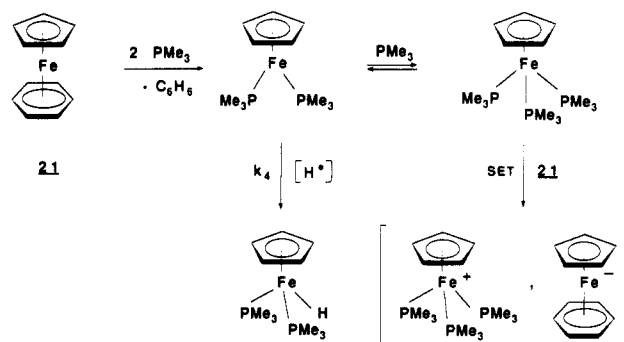
M <sup>+</sup> X <sup>-</sup> <sup>b</sup>	22 <sup>a</sup>	21 <sup>+</sup> PF <sub>6</sub> <sup>-</sup> <sup>a</sup>
without	100	0
K <sup>+</sup> PF <sub>6</sub> <sup>-</sup> = 18-crown-6	60	40
K <sup>+</sup> PF <sub>6</sub> <sup>-</sup>	30	70
Na <sup>+</sup> PF <sub>6</sub> <sup>-</sup>	0	100

<sup>a</sup> Percent of 22 and 21<sup>+</sup>PF<sub>6</sub><sup>-</sup> determined by weight (reactions are immediate). <sup>b</sup> Concentrations of both 21 and the salt in THF (30 mL) are 0.067 mol L<sup>-1</sup>; Na<sup>+</sup>PF<sub>6</sub><sup>-</sup> produces the same salt effect in DME. The intermediacy of superoxide ion is indicated by its characteristic ESR spectrum at 77 K in the reaction of O<sub>2</sub> with 21 in frozen THF solution at 150–170 K in the presence or absence of a salt.

donors in the 19e complexes [Fe<sup>I</sup>Cp(arene)] (Cp = η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>). The η<sup>6</sup> 6e arene ligand is a relatively good π acceptor whereas P ligands are poorer in this respect. Thus, the result of the replacement of toluene by three 2e PMe<sub>3</sub> donors is a shift of the E° value of the 18e/19e redox system [FeCpL<sub>3</sub>]<sup>+0</sup> (L<sub>3</sub> = toluene vs 3 PMe<sub>3</sub>) from -1.3 V to -2.05 V vs SCE. The new 19e species [FeCp(PMe<sub>3</sub>)<sub>3</sub>] is so electron rich that it may reduce the 19e complex [FeCp(toluene)] to the 20e anionic species [FeCp(toluene)]<sup>-</sup>.

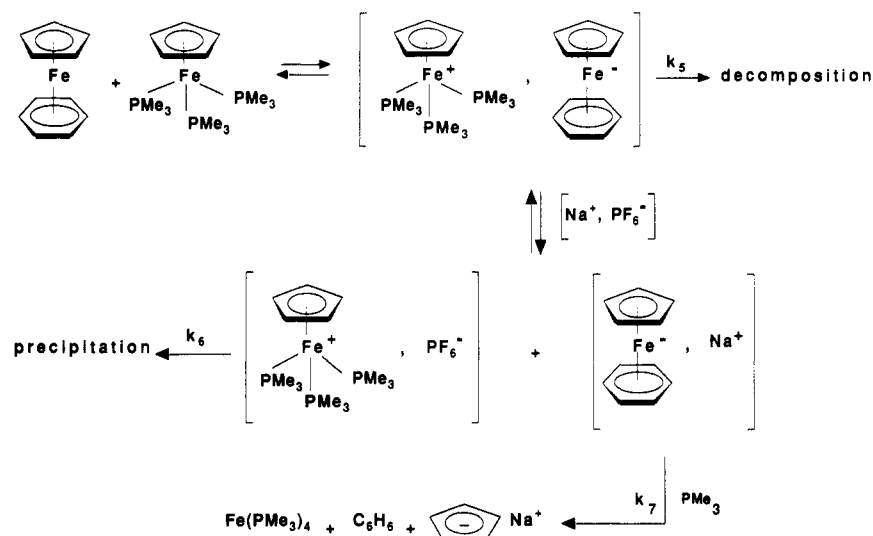
However, this reduction is not observed because the radical reaction of the 17e species [FeCp(PMe<sub>3</sub>)<sub>2</sub>] (which is in equilibrium with the 19e species [FeCp(PMe<sub>3</sub>)<sub>3</sub>]) is faster than the follow-up chemistry resulting from SET (Scheme 14).<sup>72</sup>

On the contrary, when the reaction of 21 with PMe<sub>3</sub> in THF is carried out in the presence of 1 equiv of Na<sup>+</sup>PF<sub>6</sub><sup>-</sup>, the radical reaction is not observed and [FeCp(PMe<sub>3</sub>)<sub>3</sub>]<sup>+</sup>PF<sub>6</sub><sup>-</sup>, [Fe(PMe<sub>3</sub>)<sub>4</sub>], benzene, and cyclopentadienylsodium are formed. These products all result from SET followed by metathesis of the organoiron ion pair with Na<sup>+</sup>PF<sub>6</sub><sup>-</sup> and subsequent reaction of Fe<sup>0</sup> with PMe<sub>3</sub> (Scheme 15).

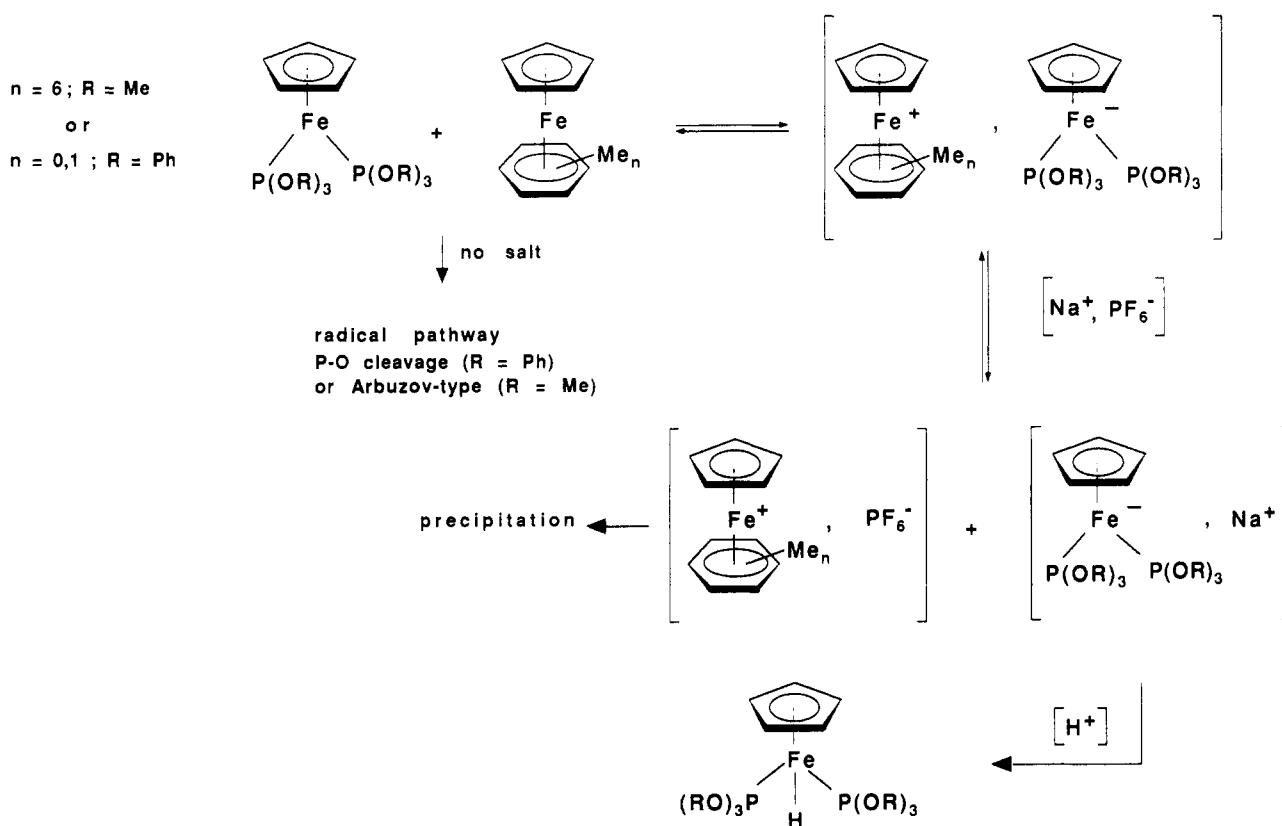
**SCHEME 14**

The thermodynamics of the metathesis reaction between the ion pairs is not in favor of the formation of the final products because the starting ion pairs have ions of closer size than those of the exchanged ion pairs. However, the reason for the salt-induced SET is found in the fast kinetics of decomposition of the ion pair [FeCp(C<sub>6</sub>H<sub>6</sub>)<sup>-</sup>, Na<sup>+</sup>] as compared to [FeCp(C<sub>6</sub>H<sub>6</sub>)<sup>-</sup>, FeCp(PMe<sub>3</sub>)<sub>3</sub><sup>+</sup>] (*v*<sub>7</sub> >> *v*<sub>5</sub>). Thus, the rate of decomposition of the 20e anion [FeCp(C<sub>6</sub>H<sub>6</sub>)<sup>-</sup>] is extremely dependent on the size of the counteranion, i.e. the large counteranion [FeCp(PMe<sub>3</sub>)<sub>3</sub>]<sup>+</sup> considerably slows down the decomposition and the small cation Na<sup>+</sup> accelerates it. Under these conditions, *v*<sub>7</sub> >> *v*<sub>4</sub>, i.e. the decomposition of [FeCp(C<sub>6</sub>H<sub>6</sub>)<sup>-</sup>, Na<sup>+</sup>] is much faster than the radical reaction of [FeCp(PMe<sub>3</sub>)<sub>2</sub>]. The thermodynamic factors associated with this system are the equilibrium between the 17e species [FeCp(PMe<sub>3</sub>)<sub>2</sub>] and the 19e species [FeCp(PMe<sub>3</sub>)<sub>3</sub>] for which precise informations are not available and the redox step which is slightly in favor of the SET in the case of PMe<sub>3</sub> (by 0.15 V). Although these thermodynamic factors are important, they can be varied to some extent without perturbing the observation of a "quantitative salt effect" in the presence of 1 equiv of Na<sup>+</sup>PF<sub>6</sub><sup>-</sup>. For instance, the same chemistry and salt effect are found with P(OMe)<sub>3</sub> instead of PMe<sub>3</sub>, although this change renders the redox step endergonic by 0.2 V. Indeed the E° of [FeCp{P(OMe)<sub>3</sub>}<sub>3</sub>]<sup>+10</sup> is -1.72 V vs SCE, i.e. lower than that of [FeCp(C<sub>6</sub>H<sub>6</sub>)<sup>0/-</sup>] (E° = -1.9 V vs SCE). This means that the presence of Na<sup>+</sup>PF<sub>6</sub><sup>-</sup> induces a thermodynamically unfavorable SET. This endergonicity can be tentatively increased by adding methyl substituents on the benzene ligand of 21 or by replacing P(OMe)<sub>3</sub> by P(OPh)<sub>3</sub> (in the latter case, the equilibrium between the 17e and 19e species [FeCp{P(OPh)<sub>3</sub>}<sub>3</sub>]<sup>+n</sup> (*n* = 2, 3) is also displaced toward the 17e species for steric reasons). With [FeCp(mesitylene)], the reaction of P(OMe)<sub>3</sub> carried out in THF in the presence of Na<sup>+</sup>PF<sub>6</sub><sup>-</sup> has to face an endergonicity of 0.4 V for the redox step, and yet, it is again quantitative. On the other hand, with [FeCp(C<sub>6</sub>Me<sub>6</sub>)] and P(OMe)<sub>3</sub> or with [FeCp(toluene)] and P(OPh)<sub>3</sub>, the endergonicity of 0.8 to 1 V cannot be overcome, and another reaction pathway is observed. In these two cases, the radical reaction is also cancelled by the presence of 1 equiv of Na<sup>+</sup>PF<sub>6</sub><sup>-</sup> and the 17e radical [FeCp{P(OR)<sub>3</sub>}<sub>2</sub>]<sup>•</sup> is reduced by the starting complex [Fe<sup>I</sup>Cp(arene)]. This salt effect (Scheme 16) is of the same nature as the one described in Schemes 14 and 15, i.e. the new ion pairs formed by ion pair metathesis with Na<sup>+</sup>PF<sub>6</sub><sup>-</sup> have a faster decomposition kinetics (for one of them) than the kinetics of the radical pathway (H-atom abstraction or Arbuzov-type).

SCHEME 15



SCHEME 16

Table 6. Yield of  $[\text{Fe}^{\text{II}}\text{CpL}_3]^+$  in the Reaction of  $[\text{Fe}^{\text{I}}\text{Cp}(\text{C}_6\text{H}_5\text{Me})]$  with  $\text{PMe}_3^a$ 

salt	$\text{NaPF}_6$	$\text{NaBF}_4$	$n\text{Bu}_4\text{NBF}_4$	$\text{KBF}_4$	$\text{KPF}_6 = 18 \text{ crown-6 (1/1)}$	no salt
yield of $\text{Fe}^{\text{II}}\text{CpL}_3^+$ , %	50	35	30	26	17	0

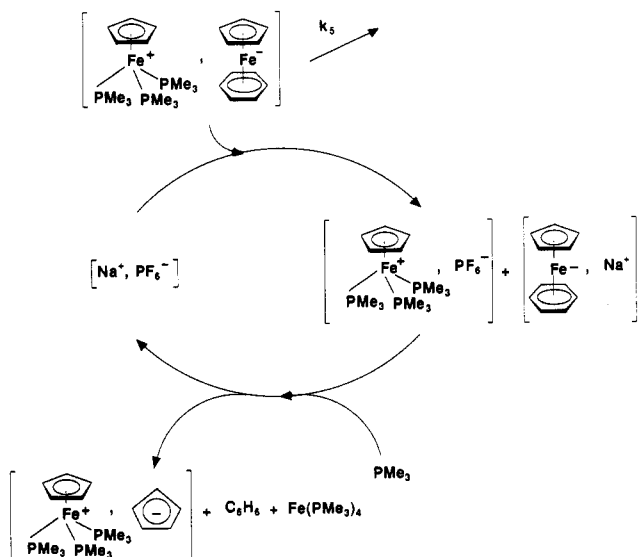
<sup>a</sup> Influence of various salts in stoichiometric amounts. The maximum theoretical yield is 50%.

It is thus striking that, whatever the thermodynamics of the equilibrium, a SET pathway is always preferred to the radical pathway observed in the absence of  $\text{Na}^+\text{PF}_6^-$ . As with the reaction system involving  $\text{O}_2$ , the sizes of the ions of the added salt were varied, and the results shown in Table 6 for the reaction between  $[\text{FeCp}(\text{C}_6\text{H}_5)]$  and  $\text{PMe}_3$  are again consistent with the salt effect. This confirms that  $\text{Na}^+\text{PF}_6^-$  is the optimum salt insuring a "quantitative" salt effect.

The influence of the precipitation was also examined as one may believe it to be crucial to the observation of the salt effect. However, such is not the case. The complexes  $[\text{FeCpL}_3]^+$ , ( $\text{L}_3 = 3 \text{PR}_3$  or arene) obtained in the cases of salt effect are essentially insoluble in THF but soluble in a THF/ $\text{Me}_3\text{CN}$  mixture (1/1). In such a medium, precipitation was indeed never observed but the reaction products were the same ( $\text{PF}_6^-$  salts), indicating that the influence of the precipitation was

not critical. Furthermore, we envisaged the possibility of recycling the salt ions in order to test the feasibility of a catalytic salt effect. Thus, in the case of the reaction between  $[\text{FeCp}(\text{toluene})]$  and  $\text{PMe}_3$  in  $\text{THF}/\text{Me}_3\text{CN}$ , we used a catalytic amount of  $\text{Na}^+\text{PF}_6^-$  (0.1 equiv) and found a virtually quantitative formation of  $[\text{FeCp}(\text{PMe}_3)_3]^+$  without a detectable product resulting from the radical pathway. The SET is thus induced quantitatively with a catalytic amount of  $\text{Na}^+\text{PF}_6^-$  (Scheme 17) confirming that the rate of decomposition of the

SCHEME 17

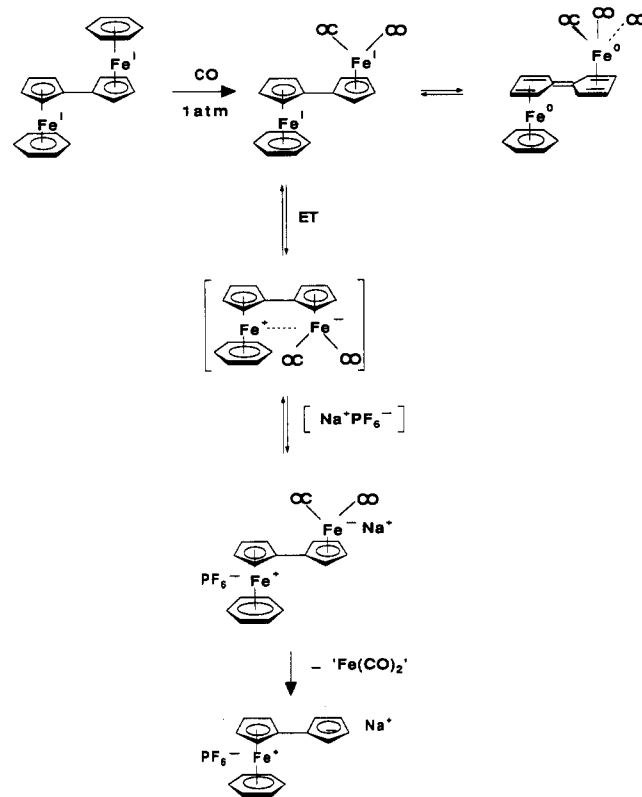


ion pair  $[\text{FeCp}(\text{C}_6\text{H}_6)^-, \text{Na}^+]$  is more than 10 times higher than that of the H-atom abstraction, itself much higher than that of the decomposition of the ion pair  $[\text{FeCp}(\text{C}_6\text{H}_6)^-, \text{FeCp}(\text{PMe}_3)^+]$ :  $\nu_5 < \nu_4 < \nu_7$ .<sup>73</sup> A catalytic salt effect of  $\text{Na}^+\text{PF}_6^-$  is also found in the disproportionation of  $[\text{FeCp}(\text{C}_6\text{H}_6)]$ , 21, in the absence of P donor. In the absence of a salt, the dimer is the main reaction product along with a minor amount of disproportionation products (Fe, benzene, and ferrocene). With a catalytic amount of  $\text{Na}^+\text{PF}_6^-$ , only the latter disproportionation products are observed. The mechanism of the disproportionation of  $[\text{Fe}^I\text{Cp}(\text{C}_6\text{H}_6)]$  catalyzed by  $\text{Na}^+\text{PF}_6^-$  proceeds as in Scheme 17 except that  $\text{PMe}_3$  is replaced by tetrahydrofuran (THF) and  $[\text{FeCp}(\text{THF})_3, \text{Cp}^-]$  spontaneously forms ferrocene; iron powder is found instead of  $[\text{Fe}(\text{PMe}_3)_4]$ . This reaction was found to occur in THF by Nesmeyanov et al.<sup>74a</sup> who overlooked the role of the salt. The THF solution used by these authors must have contained  $\text{Na}^+\text{BF}_4^-$  or  $\text{Na}^+\text{PF}_6^-$  produced in the Na/Hg reduction of  $[\text{FeCp}(\text{C}_6\text{H}_6)^+, \text{X}^-]$  ( $\text{X}^- = \text{BF}_4^-$  or  $\text{PF}_6^-$ ). Indeed in the absence of salt,  $[\text{Fe}^I\text{Cp}(\text{C}_6\text{H}_6)]$  essentially dimerizes in THF (90% yield).

In the ligand exchange of  $\text{Fe}^I$  complexes with CO, however, no salt effect is observed. Only the dimer  $[\text{FeCp}(\text{CO})_2]_2$  is obtained whether  $\text{Na}^+\text{PF}_6^-$  is present or not because the radical reaction of  $[\text{FeCp}(\text{CO})_2\cdot]$  (dimerization) is faster than SET ( $\nu_4 > \nu_5$ ). This is due to the small size of the CO ligand. On the contrary, in the related biradical  $[\text{Fe}^I_2(\text{fulvalene})(\text{C}_6\text{H}_6)]_2$ , the reaction with CO is strongly subjected to the special salt effect which dislocates a reactive zwitterion.<sup>74</sup> In the absence of  $\text{Na}^+\text{PF}_6^-$ , this biradical reacts with CO to give the exchange of the two benzene ligands with six

CO's. The unstable complex  $[\text{Fe}^0_2(\text{fulvalene})(\text{CO})_6]$  can be characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR. In the presence of 1 equiv of  $\text{Na}^+\text{PF}_6^-$ , only one benzene exchange occurs because intramolecular SET at this stage is driven by the salt (Scheme 18).

SCHEME 18



On the other hand, in the ligand exchange with  $\text{PMe}_3$ , intermolecular SET is driven by double ion exchange with  $\text{Na}^+\text{PF}_6^-$  as in the monomeric series. This indicates that both  $\text{Fe}^I$  moieties act independently since none of them are electron poor enough to be reduced by the other.

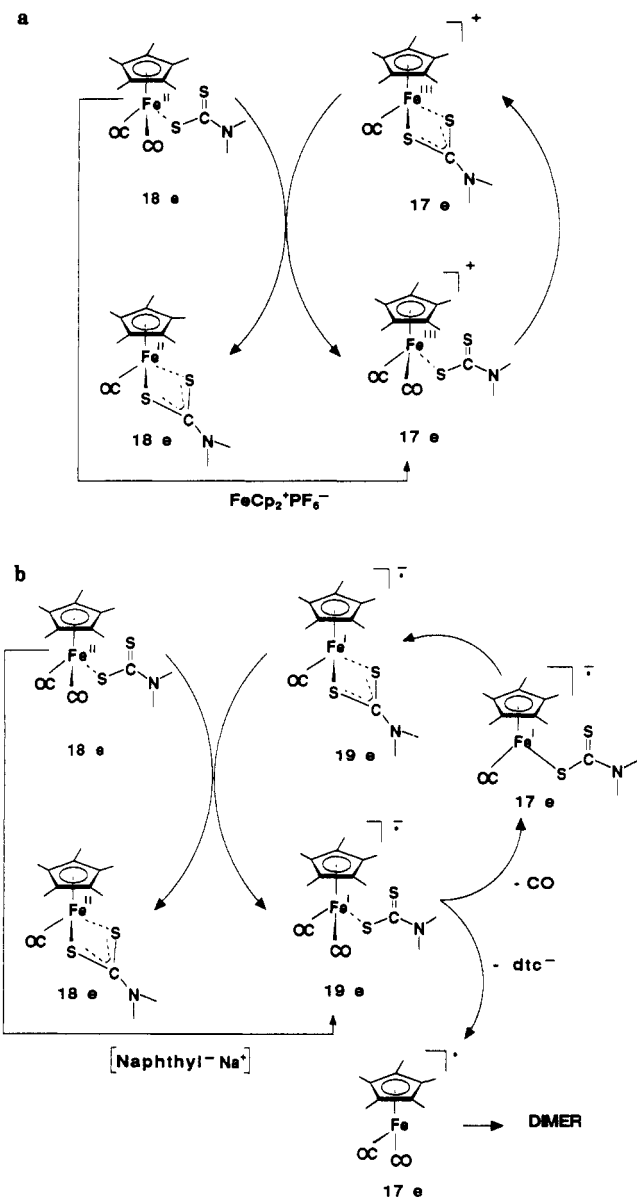
### 3. Enhancement of Coulombic Efficiency in Electron-Transfer-Chain (ETC) Catalysis

The transformation of neutral complexes by ETC catalysis involves 17e and 19e radical ions in the propagation chain.<sup>75</sup> The rate of the propagation steps depends on the counterion introduced in the initiation step. The radical ions are extremely reactive species and their side reactions are often very fast but also depend on the nature of the counterion. The ratio between the rate of the slowest propagation step and the rate of the fastest side reaction determines the Coulombic efficiency and is thus very dependent on the nature of the counterion. Analogously, the addition of an external salt provokes double ion exchange which introduces another counterion for the reactive radical ions. Therefore Coulombic efficiency is influenced. The ETC-catalyzed chelation of the monodentate dithiocarbamate ligand in  $[\text{FeCp}^*(\text{CO})_2(\eta^1\text{-SC}(\text{S})\text{NMe}_2)]$  can be initiated either by an oxidant<sup>76</sup> or a reductant.<sup>77</sup> In both cases, the nature of the counterion of the initiating redox reagent has a dramatic effect on coulombic efficiency.

In the case of the oxidative initiation (Scheme 19a), the propagation is limited by the endergonic (thus slow)



SCHEME 19



cross redox step. The competitive side reaction is the precipitation of the 17e chelated cation which is all the faster as the counteranion, introduced as a ferricinium salt, is smaller. In the reductive initiation (Scheme 19b), the propagation cycle is limited by the selectivity of ligand cleavage in the 19e anion  $[\text{FeCp}^*(\text{CO})_2(\eta^1\text{-SC}(\text{S})\text{NMe}_2)]^-$ . With  $\text{Na}^+$  as a counteranion (introduced as naphthyl sodium in the initiation), the selectivity (66%) is much better than with the large, soft counteranion  $\text{FeCp}(\text{C}_6\text{Me}_6)^+$  (introduced as the 19e  $\text{Fe}^{\text{I}}$  neutral complex in the initiation). For the latter, the selectivity is zero. The side reaction is quantitative: cleavage of the  $\text{dtc}^-$  ligand. It is probable that this difference is due to the selective binding of the hard site, the carbonyl oxygen by the hard Lewis acid  $\text{Na}^+$  assisting the cleavage of this carbonyl ligand whereas the large organoiron counteranion drives the precipitation of its  $\text{dtc}^-$  salt. A systematic study of the counterion effects in organic and inorganic ETC-catalyzed reactions, so far overlooked, will probably contribute to improve their efficiency in the future by addition of external salts and careful choice of counterions.

## B. Light-Induced SET Reactions

The area of ET photochemistry has been the subject of considerable interest recently.<sup>7,78-93</sup> Many endergonic ET reactions can be driven by light if one of the reactants absorbs in the suitable wavelength range. The gain of driving force is equal to the energy of absorption whether the excited molecule is the oxidizing or the reducing species. Both the oxidizing and reducing powers are increased by the excitation energy  $\Delta G_{\text{A} \rightarrow \text{A}^*} = n\mathcal{F}E_{\text{A} \rightarrow \text{A}^*}$ . This increase of redox power can be enormous. For benzene which absorbs in the UV region,  $E_{\text{A} \rightarrow \text{A}^*}$  reaches 4.7 V, but the ground-state redox properties of this molecule are also very weak. For most aromatic ketones, aryl olefins, and polyaromatics,  $E(\text{A} \rightarrow \text{A}^*)$  is still between 3 and 4 V (for both the singlet and triplet states). In this way, ET processes which

$$E^\circ_{\text{A}^*/\text{A}^-} = E^\circ_{\text{A}/\text{A}^-} + E_{\text{A} \rightarrow \text{A}^*} \quad (\text{eq 65a})$$

$$E^\circ_{\text{A}^*/\text{A}^+} = E^\circ_{\text{A}/\text{A}^+} + E_{\text{A} \rightarrow \text{A}^*} \quad (\text{eq 65b})$$

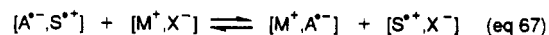
would be endergonic in the ground state become exergonic upon excitation to the excited singlet or triplet state. According to Marcus theory,<sup>69</sup> the rate of SET being given by

$$k_{\text{ET}} = [K_{\text{ET}}k_{\text{A}}k_{\text{S}}]^{1/2}$$

where  $K_{\text{ET}}$  is the equilibrium constant:  $K_{\text{ET}} = e^{-\Delta E^\circ/0.06}$  at 30 °C;  $\Delta E^\circ$  is the difference between the standard thermodynamic potentials of the two redox systems; and  $k_{\text{A}}$  and  $k_{\text{S}}$  are the rate constants of self-exchange for the redox systems of A and S. It is assumed that ET occurs at a diffusion-controlled rate when the free energy change  $\Delta G^\circ$  is more negative than  $-40 \text{ kJ mol}^{-1}$ . It follows that the exergonic SET from the excited state  $\text{A}^*$  is fast, but the back-ET to the ground-state A (eq 66b) is also exergonic, thus fast.



The only way to succeed in achieving ET is to prevent the back ET by a fast reaction of the ion-pair cage  $\text{A}^{\cdot-}, \text{S}^{\cdot+}$ . Radical ions are indeed unstable and reactive but it is difficult to compete with an exergonic ET, the rate of which can approach the diffusion-control limit. Addition of an external salt to the solution can largely favor this objective.<sup>89-91,120,121</sup> Indeed double ion exchange between the two ion pairs can also be close to the diffusion-control rate if the two pairs are of the same kind, e.g. are both contact ion pairs (CIP) or both solvent-separated ion pairs (SSIP).



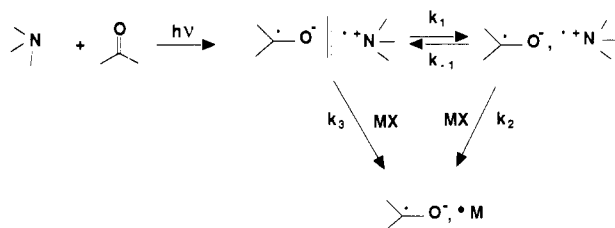
The effect of the double ion exchange is to separate  $\text{A}^{\cdot-}$  and  $\text{S}^{\cdot+}$  which slows down the back-ET and to favor their reactivities in the two new ion pairs (the reasoning is the same with  $\text{A}^{\cdot+}$  and  $\text{S}^{\cdot-}$ ).

There are now many examples of such special salt effects in the organic photochemistry of neutral molecules A.

## 1. Photophysical Studies

Using picosecond absorption spectroscopy, Peters et al.<sup>6,7,94,95</sup> studied the influence of sodium salts on the ion pairs generated during the photoreduction of benzophenone by amines (Scheme 20).

SCHEME 20



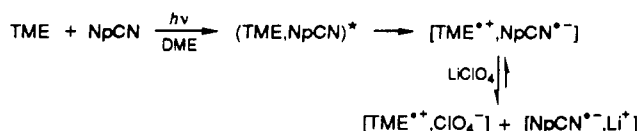
The salts NaClO<sub>4</sub> and NaI were used because of their propensity to form SSIP and CIP ion pairs respectively in acetonitrile.<sup>6,7,25a,150</sup> It was thus shown that the rate of ion-pair exchange is at a maximum when the two ion-pair structures are of the same type. The same spectroscopic study was also used to examine solvent effects on these ion-pair exchange reactions and revealed a great dependence on the solvent. In DMSO, no exchange is observed between NaClO<sub>4</sub> and the amine-ketone ion pair, the exchange process being sensitive to acceptor solvents.

Goodman and Peters used time-resolved photoacoustic calorimetry to study the effects of added salts on the ion pairs formed by photoreduction of benzophenone by DABCO.<sup>96</sup> They determined the heats of reaction in the absence and in the presence of added salts, showing thus the solvent and salt dependence for ion-pair energetics.

In recent publications, Devadoss and Fessenden<sup>13</sup> questioned the results of Simon and Peters. Using both nano- and picosecond laser photolysis, they have shown that the initial step, in all solvents, is ET to form a contact ion pair (CIP) in the triplet state. In nonpolar solvents, the ion pair remains in this form until it decays. For polar solvents, due to solvation changes, the ion pair becomes SSIP. The lifetime of the ion pair varies greatly with the solvent. Contrary to the report by Simon and Peters, the observations support the idea of a transformation from CIP to SSIP.

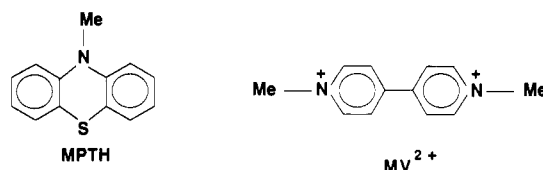
McCullough and Yeroushalmi<sup>97</sup> examined the fluorescence quenching of a series of methylnaphthalenes by substituted olefins and the effect of added salts. Exciplex fluorescence from 1-naphthonitrile (NpCN) and tetramethylethylene (TME) in DME and *t*BuOH (both solvents of medium polarity) is quenched by LiClO<sub>4</sub> or nBu<sub>4</sub>NBF<sub>4</sub> and the exciplex lifetime is shortened, suggesting that ion pairs are formed from the exciplex (Scheme 21). Tazuke et al.<sup>98</sup> showed that

SCHEME 21



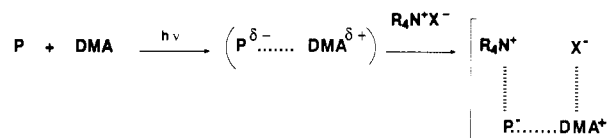
emissions of the exciplex pyrene *N,N*-dimethylaniline (DMA) is quenched by quaternary ammonium salts according to a Stern–Volmer relationship. This was taken into account by a bimolecular quenching pro-

CHART 2



ceeding with association in a quadrupole ion (Scheme 22). Hartley and Faulkner<sup>99</sup> proposed that such multiple ions or aggregates are “chemical derivatives” of the primary exciplex.

SCHEME 22

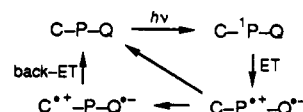


Goodson and Schuster<sup>100</sup> found that quenching of the 1,4-dicyanobenzene by nBu<sub>4</sub>NBF<sub>4</sub> in DME solution depends on the concentration. Radical ions are formed at 0.05 M salt but not at a lower concentration. It was proposed that ion-pair exchange producing free ions occurs through formation of an aggregate and a quadrupolar salt. The inhibition of back-electron transfer has been shown for instance in the photooxidation of Leuco Crystal Violet (LCV) to Crystal Violet (CV<sup>+</sup>), although micelles or polyelectrolytes are considered as the best additives.<sup>101–103</sup> Tazuke et al.<sup>102</sup> also showed that the fluorescence of the *N*-methylphenothiazine (MPTH)/methylviologen (MV<sup>2+</sup>) exciplex (Chart 2) is affected by the addition of salts only if these salts bear long alkyl chains.

The change of solvation found responsible for inhibition of back-ET within the geminate ion pair was explained by the concepts of “solvent friction” and “solvation mode”. Tazuke et al. have proposed methods to improve the quantum efficiency of such charge separation in homogeneous systems.<sup>103</sup>

Gersdorf and Mattay used flash photolysis to determine the fraction of CIP and SSIP formed by ET from triplet fluorenone to tetraethoxyethylene.<sup>104</sup> The variation of this fraction as a function of the concentration of added LiClO<sub>4</sub> shows the equilibrium between the CIP and SSIP. The study of the influence of a salt on the intramolecular charge separation was studied by Moore et al.<sup>105</sup> in the photolysis of a molecular assembly C–P–Q consisting of a tetraarylporphyrin (P) covalently linked to a carotenoid (C) and a quinone (Q). Irradiation of the porphyrin chromophore by visible light induces a rapid ET (<100 ps) to give the zwitterion C<sup>+</sup>–P–Q<sup>•-</sup> but only at high concentration of nBu<sub>4</sub>NBF<sub>4</sub> (Scheme 23).

SCHEME 23



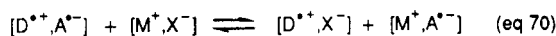
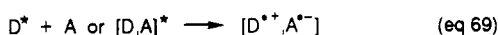
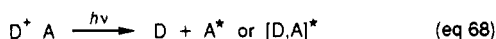
Photoredox quenching of excited [Ru(bipy)<sub>3</sub>]<sup>2+</sup> by methylviologen Ti<sup>III</sup> and Hg<sup>II</sup> was shown to be affected by the electrolyte and by the nature of the anion<sup>106</sup> (vide infra § 2 VI).

Yasuda et al.<sup>107</sup> performed kinetic studies of the decay of phenanthrene-*p*-diacyanobenzene exciplex with  $\text{PrNH}_2$  in the presence or absence of  $\text{nBu}_4\text{N}^+\text{BF}_4^-$ .

Pines and Huppert<sup>108</sup> demonstrated that addition of a salt ( $\text{NaNO}_3$  or  $\text{KNO}_3$ ) enhances the average dissociation rate of photoacids such as 8-hydroxypyrene-1,3,6-trisulfonate. By measuring the variation of photoacid quantum yields as a function of the salt concentration, they showed the geminate recombination role in deprotonation reactions. The lifetimes measured by picosecond time-resolved spectroscopy (PTRS) are shorter than those found by relative quantum yield experiments (RQY) because PTRS gives the initial deprotonation rates whereas RQS measures the average geminate recombination rate.

## 2. Photolytic Reactions Favored by the Addition of a Salt

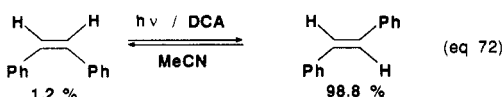
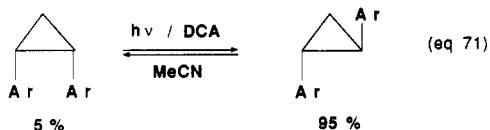
In a number of reactions, the radical cation produced by oxidation of the photoexcited state or from the exciplex is the reactive species. In these cases, an added salt induces double ion exchange which prevents the exergonic back-ET reaction. Thus the added salt enhances the quantum yield and efficiency of the light-driven reaction. All these positive salt effects follow a common mechanism:



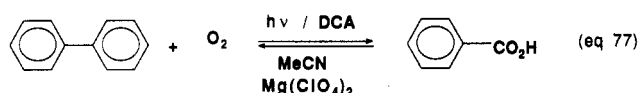
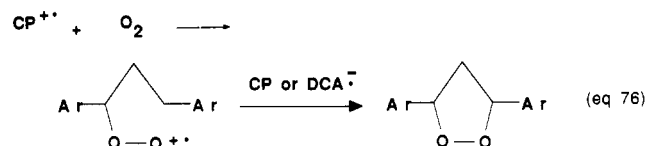
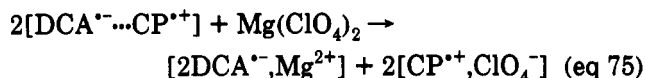
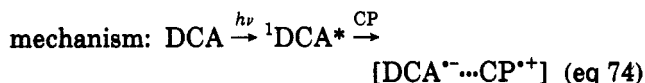
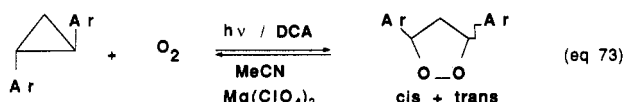
↓  
reaction

D = donor; A = acceptor (sensitizer);  $\text{M}^+\text{X}^-$  = added salt

**a. Photoisomerization.** The quantum yield of photoisomerization of *cis*-cyclopropanes (eq 71) sensitized by 9,10-dicyanoanthracene (DCA) is markedly enhanced in the presence of  $\text{Mg}(\text{ClO}_4)_2$  or  $\text{LiBF}_4$ .<sup>109</sup> Such is also the case for the photoisomerization of *cis*-stilbene to *trans*-stilbene (eq 72), favored by addition of 3–10 equiv of  $\text{NaClO}_4$ , and for the photoisomerization of *cis*-1,2-bis(*p*-methoxyphenyl)cyclopropane, favored by addition of  $\text{Mg}(\text{ClO}_4)_2$ .<sup>110–112</sup>



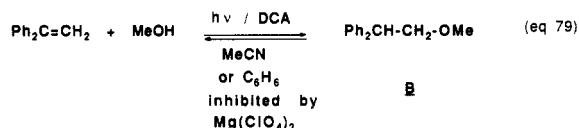
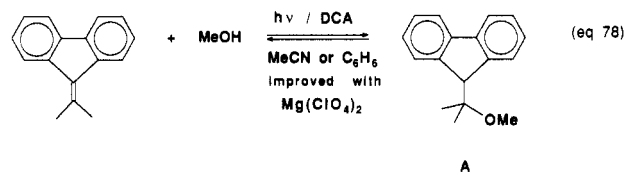
**b. Photooxidation.**<sup>113–117,154</sup> Mizuno et al.<sup>113</sup> also showed that the photooxidation of 1,2-diarylcyclopropanes (CP) (eq 73) and biphenyl (eq 77) occurs with better yields in the presence of  $\text{Mg}(\text{ClO}_4)_2$  or  $\text{LiBF}_4$ .



The oxidative photocleavage of 1,2-bis(*p*-methoxyphenyl)cyclobutane is accelerated in the presence of  $\text{Mg}(\text{ClO}_4)_2$ . No salt effect was found for 1,2-diphenylcyclobutane because the very fast back-ET prevents interaction with the salt ion pair.<sup>117</sup>

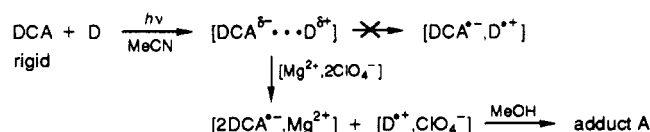
**c. Photoreduction.** The addition of  $\text{Mg}(\text{ClO}_4)_2$  accelerates the  $[\text{Ru}(\text{bipy})_3]^{2+}$ -photosensitized reduction of electron-deficient olefins by a NADH model, 1-benzyl-1,4-dihydronicotinamide. It was proposed that this effect is due to the favorable interaction of the olefin radical anion with  $\text{Mg}^{II}$ .<sup>118</sup>

**d. Photoaddition.** The DCA-sensitized photoaddition of methanol to diarylalkenes gives the anti-Markovnikov type adducts.<sup>119</sup> If the diarylalkene is rigid (9-alkylidenefluorene), the reaction is favored in the presence of  $\text{Mg}(\text{ClO}_4)_2$  in MeCN (eq 78), whereas it is not the case for the photoaddition to flexible diarylalkenes (eq 79).



This difference in salt effect is taken into account by the structural dichotomy of the diarylalkene radical cation attacked by  $\text{MeO}^-$ . The stable exciplex formed between DCA and a conformationally rigid alkene is not attacked by  $\text{MeO}^-$  (Scheme 24). However, its

### SCHEME 24

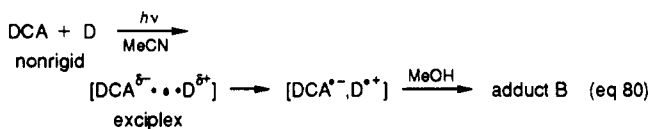


interaction with  $\text{Mg}(\text{ClO}_4)_2$  leads to the formation of  $\text{Ar}_2\text{CH}-\text{C}^+\text{Me}_2$  which correctly reacts with  $\text{MeO}^-$  to give the addition product. On the other hand, in the case of nonrigid diarylalkenes, this reaction proceeds with the geminate ion pair in which the positive charge is

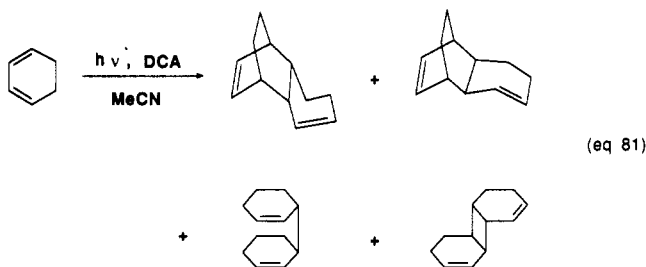
**Table 7. Results of Salt Concentration Dependence for Tropinone Photooxidation**

[LiClO <sub>4</sub> ], equiv	R <sub>2</sub> NH, %	R <sub>2</sub> NCHO, %
—	35	65
0.1	70	30
0.25	100	0
0.50	80	20
1	50	50

localized on the olefin part, owing to distortion (eq 80).

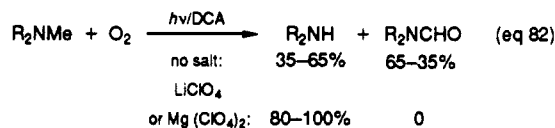


The salt inhibits this reaction because it dissociates the geminate radical ion pair to give the SSIP. Radical-cation cyclodimerizations of electron-rich 1,3-dienes and radical-cation Diels–Alder reactions of these dienes with electron-rich olefins are photosensitized by DCA, 1,4-dicyanobenzene, or fluorenone (eq 81). These reactions



have been shown by Mattay et al. to be favored by the presence of a salt (LiClO<sub>4</sub>).<sup>120,121</sup> Addition of Mg(ClO<sub>4</sub>)<sub>2</sub> increased the yield of photoaddition of 1,2-naphthoquinone with aliphatic aldehydes from 7% to 30%.<sup>149</sup>

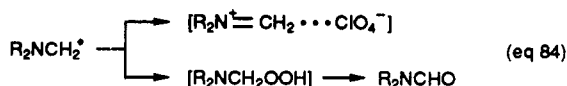
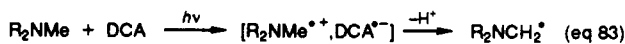
*e. Change of Selectivity in Photoadditions.* The DCA-sensitized photooxidation of tertiary methylamines was shown by Santamaria et al.<sup>122</sup> to occur according to two distinct paths. However in the presence of lithium or magnesium perchlorate, only selective N-demethylation was shown to proceed (eq 82).



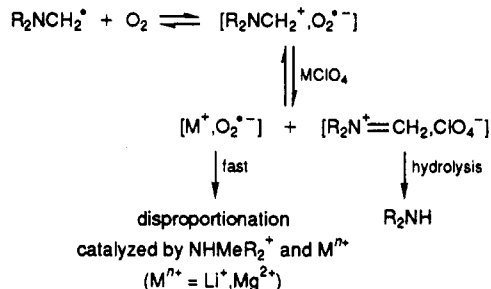
A detailed examination reveals a strong salt concentration dependence of the demethylated products (Table 7).

This reaction provides a new strategy for selective N-demethylation of tertiary methylamines with an optimal concentration of added salt.

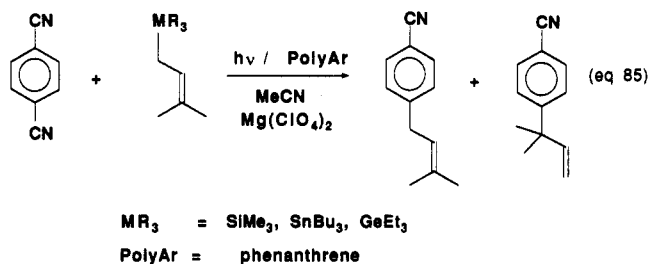
The mechanism proposed by the authors is as follows:



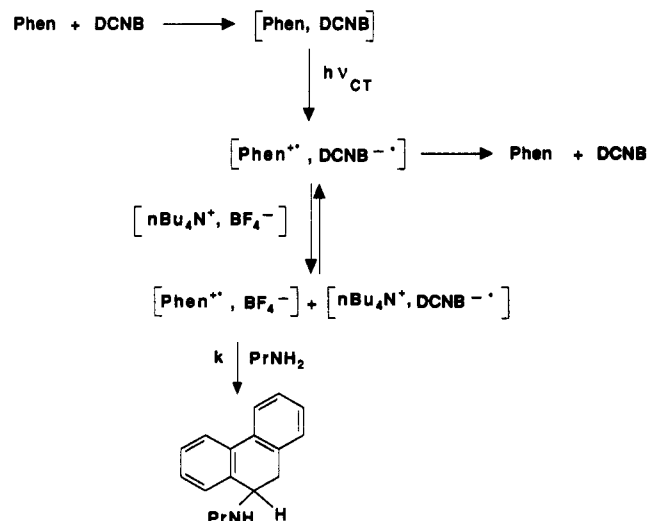
Thus it appears that a secondary ET ( $\text{R}_2\text{NCH}_2^{\bullet} \rightarrow \text{R}_2\text{NCH}_2^+$ ) is favored by the presence of the salt. One may suggest that O<sub>2</sub> is the acceptor in this oxidation and that the ET is driven by the salt-induced disproportionation of O<sub>2</sub><sup>•−</sup> (Scheme 25).

**SCHEME 25**

*f. Photosubstitution.* Mizuno et al.<sup>123a</sup> showed that the phenanthrene-sensitized substitutions of main group  $\sigma$ -alkyl organometallic complexes are accelerated in the presence of Mg(ClO<sub>4</sub>)<sub>2</sub> with increase of the quantum yield (eq 85).



Yasuda et al.<sup>107</sup> recently found that the photoamination of polyaromatics (naphthalene, 2,5-dimethylnaphthalene, anthracene, phenanthrene) sensitized by *p*-dicyanobenzene (DCNB) is only possible in the presence of tetrabutylammonium tetrafluoroborate in low polarity solvents (DME, THF, dioxane). The polyaromatic–DCNB exciplex in these solvents was observed and quenched by the salt. It was therefore concluded that the salt dislocates the geminate ion pair which provides a sufficiently long-lived polyaromatic radical cation for amination [for instance in Scheme 26, polyaromatic = phenanthrene (Phen)]. The kinetic

**SCHEME 26**

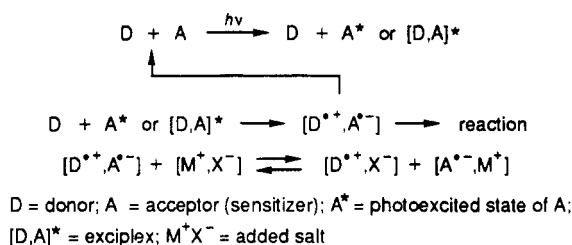
studies were performed with *p*-dimethoxybenzene used as a cation quencher and show a phenanthrene radical cation lifetime of 6–7 ns and a rate constant  $k = (6.3\text{--}11.4) \times 10^9 \text{ M s}^{-1}$  for the nucleophilic addition.

Yasuda et al.<sup>107c</sup> also studied the photosensitized oxidation of methylnaphthalenes by dicyanoanthracene. In the presence of  $\text{NEt}_4(\text{CH}_3\text{CO}_2)$ , the reaction selectivity occurs at the unsubstituted ring, whereas, in the presence of  $\text{NEt}_4\text{BF}_4$ , oxidation selectivity occurs at the substituted ring.

### 3. Photolytic Reactions Inhibited by Addition of a Salt

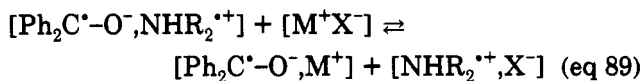
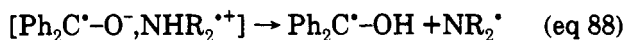
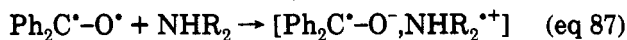
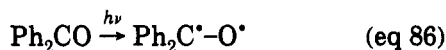
The effect of an added salt can be negative, i.e. the salt inhibits the photolytic reaction if both the radical cation and the radical anion react together within the geminate ion pair. Dislocation of the photogenerated ion pair by an added salt removes the reactive ions from each other (Scheme 27).

SCHEME 27



The known cases are the photoreduction of aromatic ketones by amines, the photoaddition of silylated tertiary amines to  $\alpha$ -enones, and the photosubstitution of anthracene.

Peters et al.<sup>6,7,94–96</sup> have shown that  $\text{NaClO}_4$  in excess considerably slows down or even inhibits photoreductions of aromatic ketones by amines. The essential steps of this reaction is ET from the amine to the ketone triplet (fast) followed by a (slow) deprotonation within the contact ion pair CIP.



The rate of this double ion exchange could be measured using picosecond spectroscopy in various solvents. It is low in coordinating solvents or even nil in the presence of a suitable crown ether. The mechanism is similar in the photoaddition of tertiary amines (Scheme 28a). In the case of  $\alpha$ -silylated tertiary amines,<sup>124–126</sup> two competing reactions can occur: deprotonation or desilylation (Scheme 28b). The ratio  $\underline{\text{A}}/\underline{\text{B}}$  markedly depends on the presence of an alkaline salt, illustrating the role of  $\text{Li}^+$  (Table 8).

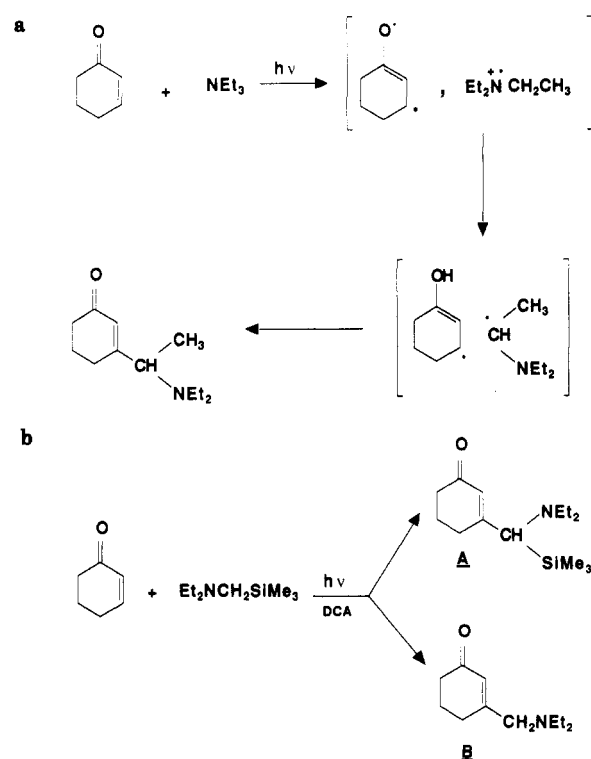
The salt effect shows that deprotonation occurs within the contact ion pair  $\underline{\text{C}}$  (eq 90) whereas it should not be the case for the desilylation (Scheme 29).

The considerable  $\text{Li}^+$  effect is caused by its large affinity for the oxoanion, both ions being hard. Thus

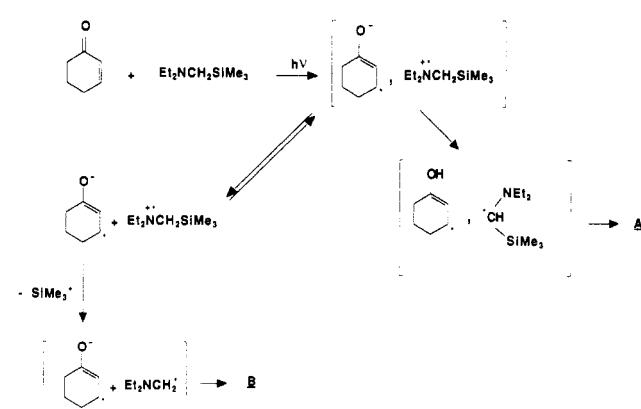
Table 8. Dependence of  $\underline{\text{A}}/\underline{\text{B}}$  on Alkaline Salt\*

salt	$\underline{\text{A}}/\underline{\text{B}}$
no salt	86/14
$n\text{Bu}_4\text{NClO}_4$ (0.48 M)	71/29
$\text{LiClO}_4$ (0.4 M)	27/73

SCHEME 28

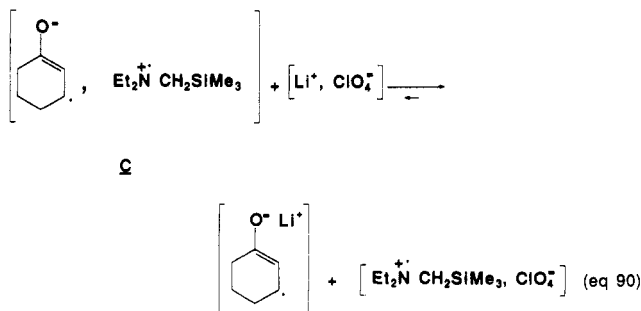


SCHEME 29



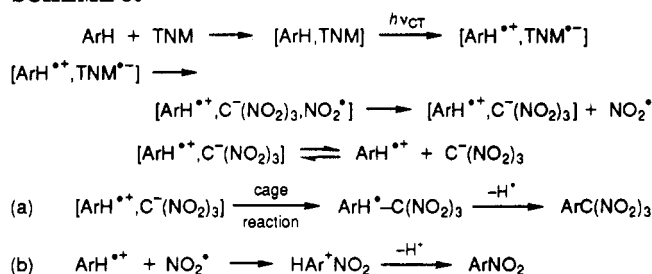
the double ion exchange is shifted toward the dislocation of the CIP  $\underline{\text{C}}$  favoring the formation of  $\underline{\text{A}}$  from a SSIP or from the free ions.

Kochi et al.<sup>127–130</sup> showed that tetranitromethane (TNM) and various aromatic donors form charge-



transfer complexes which, upon irradiation, give geminate radical ion pairs. The photogenerated species susceptible to salt effects are the  $[\text{arene}^{+\bullet}/(\text{NO}_2)_3\text{C}^-/\text{NO}_2^\bullet]$  triads and the free ions. With anthracene and *p*-methylanisole, the ion pair decay is shown in Scheme 30.

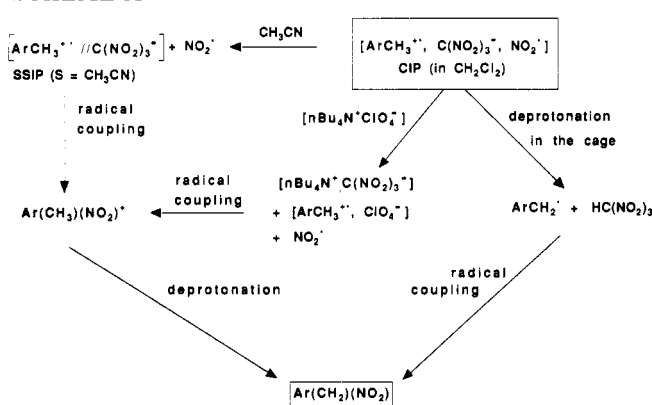
SCHEME 30



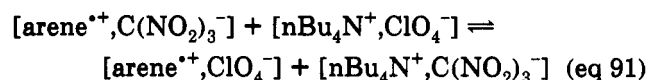
The two competing reactions (a and b) of the radical cation  $\text{ArH}^{+\bullet}$  with  $\text{C}^-(\text{NO}_2)_3$  and with  $\text{NO}_2^\bullet$  can occur. The presence of a salt, which dislocates the CIP responsible for the reaction between the two ions, inhibits this reaction a. Path b is then preferred. Solvents having a weak dielectric constant also induce the reaction a since the CIP is favored. This is the case in  $\text{CH}_2\text{Cl}_2$  ( $\epsilon = 9$ ). However, in this solvent, the reaction a is totally inhibited by the presence of  $\text{Bu}_4\text{N}^+\text{ClO}_4^-$ , and reaction b occurs. In acetonitrile, a dissociating solvent ( $\epsilon = 37.5$ ), the CIP is disrupted even in the absence of salt, and reaction b is almost exclusive under such conditions.

With polymethylbenzenes (durene and hexamethylbenzene) as the donors, a major product results from benzylic nitration according to two competing pathways (Scheme 31). In  $\text{CH}_2\text{Cl}_2$ , deprotonation occurs as the first step in a CIP as shown by the kinetic isotope effect

SCHEME 31



( $k_{\text{H}}/k_{\text{D}} \approx 3$ ). The addition of 0.2 M  $\text{nBu}_4\text{N}^+\text{ClO}_4^-$  provokes the loss of this kinetic isotope effect ( $k_{\text{H}}/k_{\text{D}} = 1$ ) because it dislocates the CIP according to eq 91.



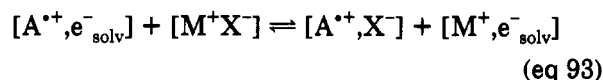
When the CIPs are dislocated, the first step is radical coupling of  $\text{arene}^{+\bullet}$  with  $\text{NO}_2^\bullet$  and deprotonation follows. This sequence is the reverse of that found with the SSIP. With the more dissociating solvent acetonitrile, the ion pairs are SSIP and radical coupling also

proceeds first; consistently no salt effect is observed upon addition of  $\text{nBu}_4\text{N}^+\text{ClO}_4^-$ .

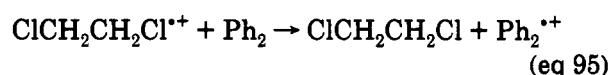
This mechanistic dichotomy disclosed by Kochi is summarized in Scheme 31.

### C. Pulse Radiolysis

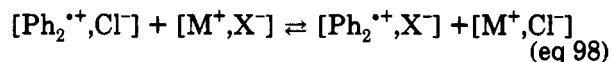
Using pulse radiolysis, molecules are oxidized by a SET and ion pairs form between the radical cation and the solvated electron (eq 92). Thus such ion pairs are extremely unstable but the radical cation can be stabilized by addition of a salt subsequent to double ion pair exchange (eq 93).



Yamamoto et al.<sup>131-135</sup> have conducted a deep and thorough study of the salt effects on the lifetimes of a series of aromatic radical cations and especially of biphenyl. Its formation and reactions under the pulse radiolytic conditions in dichloromethane are summarized in eqs 94-97.

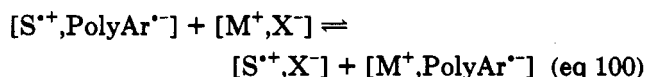
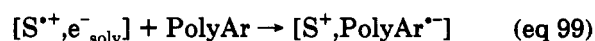


It has been shown<sup>131,132</sup> that the lifetime of  $\text{Ph}_2^{+\bullet}$  is markedly increased in the presence of a salt  $\text{M}^+\text{X}^-$  whose anions are not nucleophilic ( $\text{X}^- = \text{PF}_6^-, \text{BF}_4^-, \text{ClO}_4^-$ ). This effect was attributed to the formation of an ion pair  $[\text{Ph}_2^{+\bullet}, \text{X}^-]$  between two soft ions resulting from the exchange reaction:



The formation of the contact ion pairs  $\text{A}^{+\bullet}, \text{M}^+$  and  $\text{X}^-, \text{D}^{+\bullet}$  have been shown by the  $\text{nBu}_4\text{N}^+\text{PF}_6^-$  salt ( $\text{M}^+\text{X}^-$ ) induced blue shifts of the absorption maxima of the stilbene and diphenylpolyene radical anions  $\text{A}^{+\bullet}$  and the radical cation  $\text{D}^{+\bullet}$  of  $\alpha, \omega$ -diphenylpolyenes.<sup>133-135</sup>

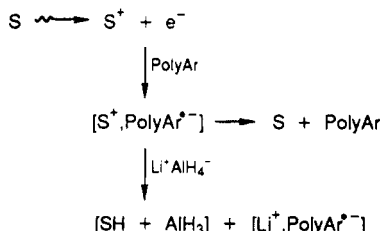
The electron detached from a solvent can be used to produce aromatic radical anions whose lifetime is increased by addition of a salt (eqs 99 and 100).



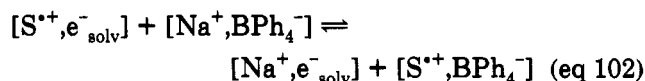
Baxendale et al.<sup>136</sup> have shown that the lifetimes of the radical anions of anthracene, pyrene, and phenanthrene generated by pulse radiolysis of THF or dioxane solutions are markedly increased in the presence of the

$\text{Li}^+$  cations from  $\text{LiAlH}_4$ . This cation stabilizes the aromatic radical anion preventing the geminate recombination. Yields of radical anions were 0.66 (pyrene $^{\cdot-}$ ) and 0.70 (anthracene $^{\cdot-}$ ) on a microsecond time scale but much higher on a nanosecond time scale. The addition of  $\text{LiAlH}_4$  led to increased reaction yields and longer lifetimes even on a microsecond time scale (Scheme 32).

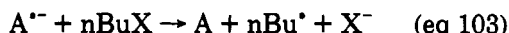
SCHEME 32



Likewise,  $\text{Na}^+$  from  $\text{NaBPh}_4$  is an excellent scavenger of  $\text{e}^-$  generated by pulse radiolysis. The decay rate of the ion pair  $[\text{Na}^+, \text{e}^-_{\text{solv}}]$  in THF is one order of magnitude slower than that of  $\text{e}^-_{\text{solv}}$ . This can be taken into account by the exchange reaction (eqs 101 and 102).



The stabilization of such radical anions by the double ion exchange also decreases the rates of their reactions with other substrates such as *n*-butyl halides. Using fast optical absorption spectroscopy, Bockrath and Dorfman reported in 1973 that the measured absolute rate constants for ET from  $\alpha$ -naphthalide radical anion and biphenyl radical anion to *n*-butyl chloride and iodide (eq 103) depend on their ion pairing with  $\text{Na}^+$ : *k*



(free ion)  $> k$  (loose ion pair)  $> k$  (tight ion pair).<sup>137-140</sup> The  $[\text{Na}^+, \text{A}^{\cdot-}]$  ion pair exhibits a reactivity that is approximately 2 orders of magnitude lower than that of the "free" radical anion  $\text{A}^{\cdot-}$ . Salmon et al. also studied pulse radiolysis of THF solutions of alkali metal cations generating solvated electrons and found enhanced yields by addition of  $\text{Na}^+$  explained as above.<sup>141-144</sup>

#### IV. Conclusion and Prospects

The special salt effect was disclosed in the pioneering work of Winstein 35 years ago.<sup>8</sup> The influence of an added salt to an ion pair participating in a chemical reaction is a very wide phenomenon whose magnitude depends on the dielectric constant of the solvent, on the nature of the interacting ionic species, and on the decay rate of the geminate ions of the ion pair.

The added salt changes the selectivity of the reaction pathway whether the ionic species are preformed substrates or are generated in the preliminary reaction step. In the latter case, the salt effect can be even more dramatic because of the formation of the CIP in solvents with a low dielectric constant. Even when the decay rate of the geminate ions of a CIP is very high, the salt

can inhibit this reaction because dislocation by double ion pair exchange between the two CIP's occurs at a diffusion-controlled rate.<sup>5</sup> Thus this special salt effect can be taken as a strong indication of a mechanism proceeding by collapse of a geminate CIP.

There are so far too few synthetic investigations such as calorimetric studies of salt effects in general<sup>153</sup> and of ion pair exchange in particular<sup>96</sup> to provide us free energies which would give a thermodynamic picture of these phenomena. Forthcoming research in this area would be enlightening.

The two major cases of generation of geminate ion pairs from neutral species, both susceptible to the special salt effect, are (i) the reaction between an electrophile and a nucleophile and (ii) ET between a donor and an acceptor. This second category includes ET in the exciplex state which has recently attracted considerable interest from a mechanistic and synthetic standpoint. The specific salt effect is so dramatic in these processes that it is now being systematically studied and used to tune desired light-induced synthetic pathways. The salt effect is all the more necessary in harvesting the benefit of ET in the exciplex state where the back-ET is exergonic. Thus the use of suitable salts to inhibit this back-ET in solar energy storage devices is also likely to be a challenging issue in the close future.<sup>89,145</sup>

Strong specific salt effects have also been shown in ETC catalysis where the radical ion intermediates provide side reactions which depend on the nature of the counterion introduced in the initiation step.<sup>77</sup> Synthetic applications of this mechanistic feature should be forthcoming.

Salt effects are found in varied areas such as ET in photosynthetic membranes,<sup>89,146</sup> photosensitized DNA oxidation,<sup>147</sup> or catalysis using zeolite cages even if mechanistic investigations are often limited by the complexity of such systems. However the potential of the *special* salt effect in biochemistry is clear as shown by the total inhibition of the cage reactivity of superoxide radical anion by sodium salts mimicking in this way the superoxide dismutase enzymes.<sup>68b,71</sup>

#### Note Added in Proof

Seki has studied the effect of various perchlorate salts on the quantum yield and decay of ions produced by photoinduced ET from zinc tetraphenylporphyrin to 1,4-benzoquinone in 4-methylpentan-2-one.<sup>155</sup>

In examining the picosecond dynamics of contact ion pairs  $[\text{An}^+, \text{T}^-]$  and  $[\text{BA}^+, \text{T}^-]$  ( $\text{T}^-$  = trinitromethide anion; An = anthracene, BA = bromoanthracene), Kochi's group has disclosed ionic exchange of the CIP with salts containing either innocuous or common ions for CIP lifetimes of  $>700$  ps.<sup>156</sup>

Salt effects on charge separation in the exciplex formed by photoamination of arenes of relatively low polarity,<sup>157</sup> on photoinduced ET isomerization of *cis*-stilbene and quadricyclane,<sup>158</sup> and on ET photooxidation of 1,4-diphenyl-1,3-butadiene have been published.<sup>159</sup>

Drastic salt effects have been found in the photosensitized oxygenation of naphthalene derivatives.<sup>160</sup> In MeCN,  $\text{LiClO}_4$  was found to influence the photoinduced ET reactions of  $\alpha, \beta$ -epoxy ketones with amines.<sup>161</sup> The DCA-sensitized photoisomerization of



*trans*- and *cis*-1,2-bis(4-methoxyphenyl)cyclopropanes in MeCN was remarkably accelerated by adding Mg-(ClO<sub>4</sub>)<sub>2</sub> or LiBF<sub>4</sub>.<sup>162</sup> The Hamon-Lapinte group found another salt effect on the reaction of electron-rich organoiron compounds with O<sub>2</sub> via O<sub>2</sub><sup>•-</sup>.<sup>163</sup>

Bockman and Kochi have reported and carefully studied a salt effect on the ET equilibria of redox-active ion pairs generated by reacting MTp(CO)<sub>3</sub><sup>-</sup> (Tp = hydridotris(3,5-dimethylpyrazolyl)borate; M = Cr, Mo, W) with the triarylpyrylium cation.<sup>164</sup>

## V. Abbreviations

A	acceptor
Ac	acetyl
AN	acceptor number
Ar	aryl
CIP	contact ion pair
CP	1,2-diarylcyclopropane
Cp	η <sup>5</sup> -C <sub>5</sub> H <sub>5</sub>
Cp*	η <sup>5</sup> -C <sub>5</sub> Me <sub>5</sub>
C-P-Q	carotenoid-tetraarylporphyrin-quinone assembly
D	donor
DCA	9,10-dicyanoanthracene
DDQ	2,3-dichloro-5,6-dicyano- <i>p</i> -benzoquinone
DCNB	<i>p</i> -dicyanobenzene
DMA	<i>N,N'</i> -dimethylaniline
DMABB	<i>p</i> -[ <i>p</i> -(dimethylamino)benzyl]benzophenone
DME	1,2-dimethoxyethane
DMF	dimethylformamide
DMSO	dimethyl sulfoxide
DN	donor number
E°	thermodynamic redox potential
e	electron
17e	17-electron
19e	19-electron
ET	electron transfer
ETC	electron-transfer chain
L	2-electron ligand
M	molar
M <sup>+</sup>	alkaline metal—or tetraalkylammonium cation
Me	methyl
MPTH	<i>N</i> -methylphenothiazine
MV <sup>2+</sup>	methylviologen
NpCN	1-naphtonitrile
P	pyrene
Ph	phenyl
Phen	phenanthrene
PolyAr	polyaromatic
Pr	propyl
R	alkyl
R <sup>+</sup>	carbocation
RM	organolithium or -sodium reagent
RX	alkyl halide
SCE	saturated calomel electrode
SET	single electron transfer

SSIP	solvent-separated ion pair
THF	tetrahydrofuran
TME	tetramethylethylene
TNM	tetranitromethane
ε	solvent dielectric constant

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