

ISOLATION, PROPERTIES AND ASSOCIATION PHENOMENA OF ALKALINE
SALTS AND THEIR CROWN COMPLEXES OF A RADICAL ANION

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ABSTRACT. The obtention of (tetradecachloro-4-oxidotriphenylmethyl)⁻
M⁺ (M=Li, Na, K, n-Bu₄N) salts in ethereal solution and the isolation
of some alkaline complexed salts (M= Li-12C₄, Na-18C₆, K-18C₆,
K(THF)₁-(H₂O)₃₋₄, n-Bu₄N) are described and discussed. The associa-
tion phenomena of these salts has been studied by electronic spec-
troscopy, osmometry and electron spin resonance. Linear correla-
tions between radii counterions and the position maxima of the electronic
spectra bands permit the study of the species present in solution
(free ions, ion pairs and quadrupolar aggregates).

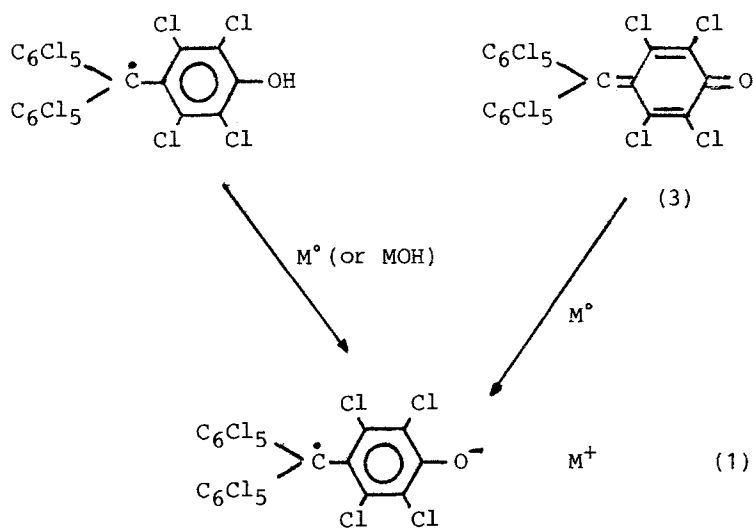
1. INTRODUCTION

Most of the existing work concerning the structure of organic anions
in solution has been performed with carbanions¹, enolates and fenoxi-
des², ketyls³ and semiquinone derivatives³. Such studies were based
principally on ESR, NMR and UV-visible techniques, and in particular
the latter have been limited to very dilute solutions in a narrow
range of concentrations, due to the very high molar extinction coeffi-
cient of the anions.

We now report a study of the structure of ionic species of a ra-
dical anion of the quinone methide type, a vinylog of a ketyl anion
radical, using UV-visible and ESR spectroscopies in a wide range of
concentrations³.

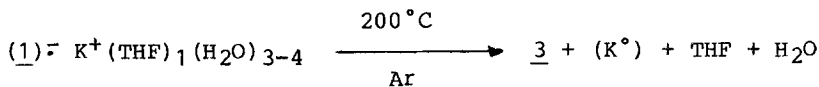
2. OBTENTION AND ISOLATION OF SALTS

Several salts of tetradecachloro-4-oxidotriphenylmethyl radical (1)
(M= Li, Na, K, n-Bu₄N) have been obtained quantitatively in ethereal
solution (diethyl ether, Et₂O; tetrahydrofuran, THF; and dimetoxi-
ethane, DME) by reaction of tetradecachloro-4-hydroxotriphenylmethyl
radical⁴ (2) with alkaline metals or hydroxides or by reduction of
perchlorofuchsona (3) with metals.



M = Li, Na, K, n-Bu₄N, Li-12C₄, Na-18C₆, K-18C₆

Solutions of salts 1 have been found to be persistent in Et₂O, THF, DME and DMSO/Et₂O and very stable toward oxygen. However, isolation of such salts in solid state is only possible when the alkaline counterion is completely solvated; i.e., K(THF)₁-(H₂O)₃₋₄, K-18C₆, Na-18C₆, Li-12C₄ or when the counterion is a poor electron acceptor like n-Bu₄N. The solvation sphere of alkaline cations is a major factor on the stabilities and even on the ionicities of such salts, as evidenced in the thermal decomposition.



Such decompositions formally imply an electron transfer from the radical-anion to potassium and is similar to those observed in perchlorotriphenylmethide salts⁵.

3. ASSOCIATION PHENOMENA

The association phenomena of salts 1 in solution - free ions (M⁺A⁻), quadrupolar ions (M⁺A⁻)₂ - have been studied by electronic spectroscopy, electron spin resonance and osmometry.

The electronic spectra of salts 1 show four bands, whose wavelength maxima and absorptivities depend on : a) Nature of counterion (Li, Na, K, n-Bu₄N), b) Solvent (Et₂O, THF, DME, DMSO/Et₂O),

c) Concentration (10^{-6} – 10^{-2} M) and d) Complexing agents (12C4, 18C6); the highest wavelength band being the most sensitive. Figure 1 shows the curves of the wavenumber for the latter band vs the concentration in Et₂O of salts 1 with different counterions. Similar curves are obtained in THF and DME.

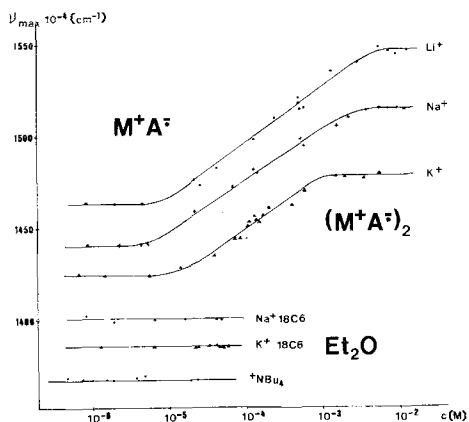


Figure 1. Dependence of wavenumber absorption maxima, $\bar{\nu}_{max}$, of salts 1 on concentration, C .

Such results can be interpreted on the basis of formation of ion pairs at lower concentrations and quadrupolar aggregates at higher ones. For both species a bathochromic shift is observed when the solvation capability of solvents is increased ($\text{Et}_2\text{O} < \text{THF} < \text{DME}$), suggesting an externally solvated species like $A^- M^+$, S_n and $(A^- M^+)_2 S_n$. The quadrupolar nature of these species at higher concentrations has been independently confirmed by osmometry and by the presence of electron-electron dipolar interaction in e.s.r. spectra. The absorption maximum of the highest wavelength band in DMSO/Et₂O is not affected neither by the counterions nor concentration indicating the presence of totally solvated ion pairs, $M^+//A^-$ (or free ions, $M^+ + A^-$). The addition of 18-crown-6 to Et₂O solutions of Na and K salts 1 gives rise to a bathochromic shift of the maxima whose positions indicate a replacement by the crown ether of the ethereal external solvation sphere on $A^- M^+$, S_n giving species like $A^- M^+ - 18C6$. By contrast 12-crown-4 is not able to perform such replacement on Li salt 1 in Et₂O, due to the higher hardness of Li.

Linear correlations between the counterion radii, $(2+r_m)^{-1}$, and the wavenumbers, $\bar{\nu}_{max}$, of the species $A^- M^+$, S_n and $(A^- M^+)_2 S_n$, in several solvents and also for the species $M^+//A^-$ (or $M^+ + A^-$) in DMSO/Et₂O have been observed (Fig. 2).

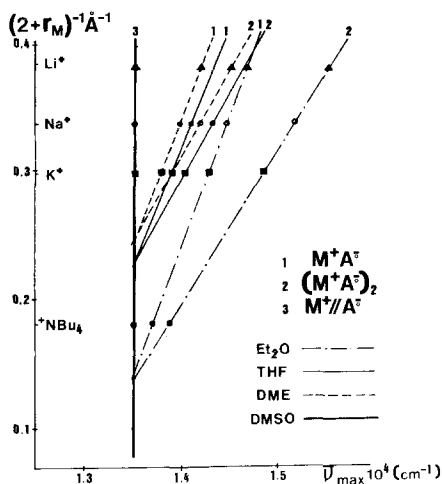


Figure 2. Linear correlations between wavenumber, $\bar{\nu}_{max}$, and cationic radii, $(2+r_m)^{-1}$ for $A^- M^+$, S_n , $(A^- M^+)_2 S_n$ and $M^+//A^-$ species.

It is remarkable that such linearity is not limited only to ion pairs and free ions as has been described elsewhere², but is possible to expand it to the quadrupolar species. Even more noticeable is that the slopes of the straight lines are similar for the ion pairs in all the studied solvents (slope $\approx 1.9 \cdot 10^4$) as occurs also for the quadrupolar ions (slope $\approx 1.3 \cdot 10^4$), being both values different from that observed for the free ions (slope = ∞). Therefore, such magnitude (slope) appears to be independent from the nature of the solvent and seems to be only dependent on the state of aggregation, reflecting the "anion susceptibility to the counterions perturbations". Thus electronic spectroscopy appears to be a reliable technique even for the identification of the state of aggregation of radical anions.

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