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CONCERNING THE ELECTROPHILIC PERCHLORATION OF ALKENES[1]

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Abstract: It is proposed that the formation of perchlorate esters from the interaction of electrophilic halides with alkenes in the presence of excess lithium perchlorate results not from some "amazing" increase in the nucleophilicity of the perchlorate ion in low polarity solvents but from the inertness of contact lithium chloride ion pairs relative to solvent separated lithium perchlorate ion pairs.

In the presence of an excess of lithium perchlorate, electrophilic additions to alkenes in low polarity solvents are frequently diverted, in part, to perchlorate esters,[2-4] formed by the initial electrophilic attack being followed by intervention of perchlorate ion. This phenomenon has been described as remarkable,[3] amazing,[3,4] and surprising,[4] and it has been discussed in terms of a breakdown of the usual theory of nucleophilicity orders.[4]

For reaction in diethyl ether, it was suggested[4] that an important consideration is that the perchlorate ion will have its nucleophilicity significantly increased on transfer from a protic to an aprotic solvent. However, the competing halide ions do not exhibit the internal charge dispersal present in the perchlorate ion and they should benefit even more by such a transfer. The increased nucleophilicity spread should actually favor capture of halide ion. It was also observed that the perchlorate ion intervenes significantly for reaction (scheme 1) of alkenes

$$RCH=CH_2 + X_2 + LiClO_4 \xrightarrow{Et_2O} RCH(OClO_3)CH_2X + RCHXCH_2X \qquad (1)$$

with Cl_2, less well for reaction with Br_2 and poorly for reaction with I_2. This was explained in terms of bromide ion having a higher nucleophilicity than chloride ion. However, it is well established that this is the case only when the ions are well solvated and in an aprotic solvent the order of intrinsic nucleophilicities ($Cl^- > Br^- > I^-$) is followed.[5] Accordingly, alternative explanations must be sought, both for the ability of perchlorate ion to compete against halide ion and for the observation that bromide ion fares better than chloride ion in this competition. In the following narrative, evidence will be presented which indicates that a low nucleophilicity for the chloride ion rather than an inexplicably high nucleophilicity for the perchlorate ion is involved.

The kinetics for S_N2 attack by lithium halides in anhydrous acetone have been rationalized[6-8] in terms of only free ions being reactive and ion pairs being unreactive. Spectroscopic[9] and conductivity[10] studies of lithium salts in acetone have indicated that the chloride forms contact ion pairs, the iodide forms ion pairs from fully solvated ions, and the bromide represents an intermediate situation. In the lower polarity solvent tetrahydrofuran, very similar in structure to diethyl ether,[4] lithium salts are only very slightly dissociated, with dissociation constants of 1.2×10^{-10} M for lithium chloride at 20°C[11] and 2.1×10^{-8} M for lithium perchlorate at 25°C.[12] Under these conditions, it is probable that nucleophilic attack is by the relatively unreactive ion pairs. As in acetone, the lithium chloride exists as tight contact ion pairs (considerably aggregated),[13] but the lithium perchlorate exists as solvent-separated ion pairs;[14] one would expect the looser associated perchlorate ion to retain a greater proportion of its intrinsic nucleophilicity. Further, if (as in acetone[9,10]) the lithium salt ion pair becomes looser (and the anion less deactivated) as one increases the size of the halide ion, the abilities to intervene could well be $I^- > Br^- > Cl^-$, as observed.

The observation[15] that perchlorate esters are prepared in excellent yield by heterogeneous reaction of silver perchlorate with an alkyl halide in a saturated hydrocarbon solvent, despite the build up of a heterogeneous phase of silver halide, lends support to the rationalization outlined above. Finally, it is possible that the increased electrophilicity of the reagent (EX) in the presence of lithium perchlorate (the "doping" effect[16]) results in part from a specific association of lithium ion with the incipient halide ion, as in scheme 2. The electrophilic

$$\mathrm{EX} + \mathrm{Li}^+||\mathrm{ClO_4}^- \rightleftharpoons \mathrm{EX{-}{-}{-}{-}Li}^+||\mathrm{ClO_4}^- \xrightarrow{\text{alkene}} (\text{alkene E})^+\mathrm{X}^-\mathrm{Li}^+||\mathrm{ClO_4}^- \qquad (2)$$

perchloration would then parallel the familiar[17] use of halogen plus silver salt in the addition to an alkene of halonium ion plus the anion of the silver salt.

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