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CONCENTRATION AND SUBSTRATE DEPENDENT REACTION MECHANISMS IN THE METAL KETYL-ALKYL HALIDE SYSTEM. MAGNETOCHEMICAL ZERO-ORDER KINETICS AS EVIDENCE FOR A DIAMAGNETIC REACTIVE SPECIES AT HIGH KETYL CONCENTRATIONS. CATALYSIS BY TRANSITION METALS

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Metal ketyls in solution can react with alkyl halides according to a mechanism which can vary with the concentration of the ketyl and the reactivity of the halide . One of the main reasons that this effect remained obscure may be the failure to study ketyl reactions under conditions of ketyl concentrations varying within a wide range[1] . Solutions of metal ketyls contain a multitude of species which differ in the degree of association , the type of ion pairing, the magnetic state and, most probably , in reactivity . The relative amount of these species might as well be concentration dependent[2] . We report here results on magnetochemical kinetic measurements[3] at ketyl concentrations of the order of 1 M . These results differ from those reported by others[1] .

Decay of paramagnetism in lithium benzophenone ketyl ($Li^+Ph_2C{=}O^{\dot{-}}$) and Lithium fluorenone ketyl ($Li^+Fl{=}O^{\dot{-}}$) in the presence of Bu^nBr and $PhCH_2Cl$, respectively , follows zero-order kinetics (Fig.1 , lines A and B) . With the more reactive substrates EtI and Ph_2CHCl the respective change obeys first-order kinetics (Fig.1 , lines C and D) . It must be emphasized that first-order kinetics were obtained under conditions of strict stoichiometric concentrations of (ketyl:halide) 2:1 . Hence this effect is real .

Magnetic titration[3] (fig.2) results indicate that indeed the stoichiometry of the reaction is 2:1 , a ratio which has been always assumed[4] but had never accurately been determined so far[5] .

The different kinetic behaviour of a given ketyl (e.g. $Li^+Ph_2C{=}O^{\dot{-}}$) towards two substrates which differ markedly in their reactivities (e.g. EtI , Bu^nBr) can be taken as evidence for the existence of at least two ketyl species which vary significantly in their reactivities . The occurence of a diamagnetic species which exhibits a higher reactivity towards alkyl halides than any other paramagnetic species , can explain the zero-order kinetics . This species could be produced in a reversible step from paramagnetic ones . The reversible step becomes rate determining in cases where the substrate halide is of low reactivity , capable of discriminating between the ketyl species of varying reactivity. A different situation could occur with a reactive halide which can react with paramagnetic species faster than the paramagnetic-diamagnetic equilibrium can be established .

One of the few (?) possible diamagnetic species that could be involved in the reaction is the dianion $Ar_2C{=}O^{=}Li_2^{++}$. Reaction between the dianion and a halide of low reactivity could result to an increase in paramagnetism :

$$Ph_2C{=}O^{=} + Bu^nCl \longrightarrow Ph_2C{=}O^{\dot{-}} + Bu^n\cdot + Cl^-$$

Actually $Ph_2C{=}O^{=}Li_2^{++}$ was found to react very readily even with Bu^nCl in THF , but no increase in the paramagnetism of the solution was observed[6] .

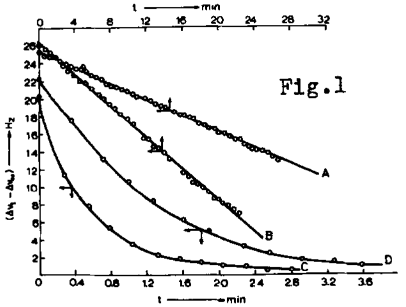
Fig.1

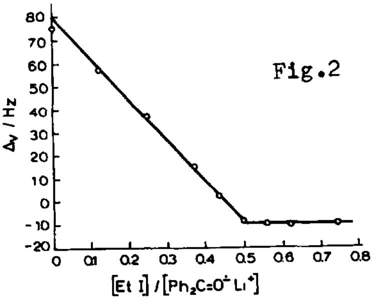
Fig.2

Fig.1 : Decay of paramagnetism in $Li^+Ar_2C{=}O^{\dot{-}}$ - RX systems . A: $Li^+Ph_2C{=}O^{\dot{-}}$ - Bu^nBr ; B: $Li^+Fl{=}O^{\dot{-}}$ - $PhCH_2Cl$; C: $Li^+Ph_2C{=}O^{\dot{-}}$ - EtI ; D: $Li^+Fl{=}O^{\dot{-}}$ - Ph_2CHCl

Fig.2 : Magnetic titration of $Li^+Ph_2C{=}O^{\dot{-}}$ against ethyl iodide .

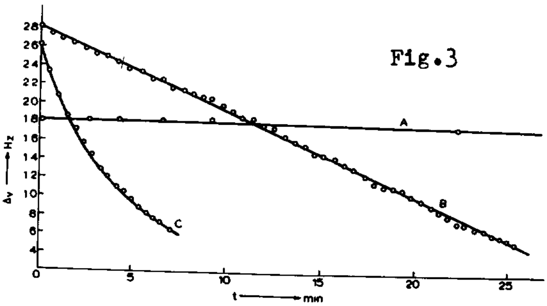
Fig.3

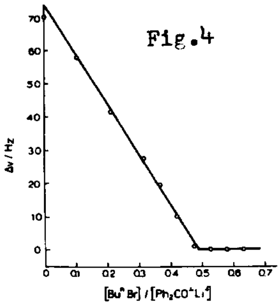
Fig.4

Fig.3 : $NiCl_2$ catalyzed reaction of $Li^+Ph_2C{=}O^{\dot{-}}$ with Bu^nCl .
A: 4% mole ; B: 10% mole catalyst ; C: no additives .
Fig.4 : Magnetic titration of $Li^+Ph_2C{=}O^{\dot{-}}$ against Bu^nBr in the presence of nickel chloride .

A pronounced catalytic effect by transition metals was observed with the least reactive halides [7] (chlorides with $Li^+Ph_2C{=}O^{\dot{-}}$ and bromides with $Li^+Fl{=}O^{\dot{-}}$). The chlorides of Cu^{I}, Co^{II}, Ni^{II} and Pd^{II} amongst other metal salts and complexes tested have a remarkable catalytic effect in this reaction . With $NiCl_2$ for example , (Fig.3) the half life is reduced to a few minutes , whereas the uncatalyzed reaction is so sluggish that it did not reach completion during a six month period ! It is noteworthy that the accelerating effect of an increased amount of catalyst is accompanied by a change in mechanism (lines B and C). This is in accord with the explanation given above . Alternatively , this could be due to the possibility that the catalyst , under these conditions becomes a co-reactant .

The product of the catalyzed reaction ($Li^+Ph_2C{=}O^{\dot{-}}$, Bu^nCl , $NiCl_2$) was shown to be a mixture of benzhydrol , benzophenone and butyldiphenyl carbinol at a molar ratio of 1:1.7:2.8 , respectively , and only trace amounts of O-alkylation product :

$$Li^+Ph_2C{=}O^{\dot{-}} + Bu^nCl \xrightarrow{NiCl_2} Ph_2C{=}O + Ph_2CHOLi + Ph_2(Bu^n)COLi$$

Thus the reaction resembles , at least qualitatively , that of $Ph_2C{=}O + Bu^nLi$ [8] .

Magnetic titration of $Li^+Ph_2C{=}O^{\dot{-}}$ against Bu^nBr , in the presence of $NiCl_2$ indicated a stoichiometry of ketyl:halide 2:1 [9] (Fig.4) .

Equivalent (2:1) ketyl:$NiCl_2$ quantities react rapidly with evolution of heat apparent discharge of the ketyl and reduction of the nickel chloride . This mixture was found to be ineffective in bringing about reduction of n-hexyl chloride . This result suggests that in some fundamental reaction step both the catalyst and the ketyl are involved simultaneously .

The data presented in this letter clearly indicate that in order to gain a thorough understanding of the chemistry of ketyls , detailed kinetic studies are needed , especially at high ketyl concentrations . An investigation of the chemistry of diamagnetic species which possibly take part in the complex equilibria of metal ketyl solutions may also prove to be of value . As far as the catalytic effect is concerned , we anticipate that it could be generally operable in the reactions of radical anions as well as in dissolving metal reactions Perhaps the oldest known example of this type of catalysis is the ferric ion catalyzed amidation of alkali metals dissolved in liquid ammonia[10] .

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REFERENCES AND NOTES

1. Reported kinetic studies were limited to dilute , up to 10^{-3} M , ketyl solutions . Rate measurements were carried out under pseudo-first-order conditions . E.Warhurst and R.Whittaker, Trans.Faraday Soc., 62, 707 (1966), and references therein .
2. For reviews see N.Hirota, 'Radical Ions' E.T.Kaiser and L.Kevan,Editors , Wiley-Interscience, New York 1968 , p.35 ; J.Smid, 'Ions and Ion Pairs in Organic Reactions', M.Szwarc, Editor, Wiley-Interscience, New York 1972 p. 145 .
3. C.G.Screttas , J.C.S.,Perkin II, 745 (1974) ; Chem.Commun. 869 (1972) .
4. D.J.Morantz and E.Warhurst, Trans.Faraday Soc., 51, 1375 (1955) .
5. Ratios deviating significantly from 2:1 were obtained with Bu^nBr . However , long reaction times which were necessary for measuring residual paramagnetism , made the results unreliable .
6. This result cannot be taken as a negative evidence against the involvement of the ketone dianion .
7. The alkyl chlorides and bromides used in this work were purified as described in reference 4 .
8. See for example , C.G.Screttas , Abstracts VIth International Conference on Organometallic Chemistry, Amherst Mass.,Aug. 13, 1973 No. 26 .
9. Normal butyl chloride gave non-reproducible results , see note 5 .
10. T.H.Vaughn, R.R.Vogt and J.A.Nieuwland, J.Am.Chem.Soc., 56, 2120 (1934) .