The Influence of σ–π Conjugation on the Rate of Protodemetallation Reactions†

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Summary σ–π Conjugation is responsible for the large increase in the rate of protodemetallation reactions of R_3MPh when M is varied from C to Pb in the Group IV series.

THE recent publication on *ipso* directive effects in electrophilic aromatic substitution reactions[1] has prompted us to report an *ipso* effect of unusual magnitude, and simul-

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†Abstracted in part from the Ph.D. thesis of the author, University of California at San Diego, 1970.

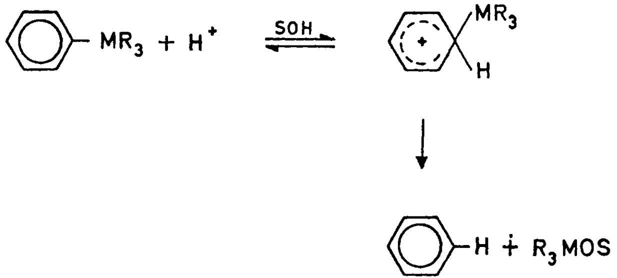
M	ν_{CT} (Ph_3MCH_2Ph)^a (cm^{-1} × 10^{-3})	σ^+_{CT} (Ph_3MCH_2–)^a	k_{rel} (Et_3MPh)^b	σ^+_{calc} (Et_3MCH–)^c
C	23·7	−0·24	1	—
Si	22·2	−0·42	10^4	−0·6
Ge	20·7	−0·60	10^6	−0·8
Sn	18·8	−0·81	10^{10}	−1·3
Pb	17·1	−1·1	10^{13}	−1·7

[a] For experimental details and calculation of σ^+_{CT}, see Ref. 4; [b] Ref. 2; [c] Assuming σ^+ (Et_3MCH–) = σ^+ (Me_3SiCH_2) = − 0·6 as calculated from data in ref. 6.

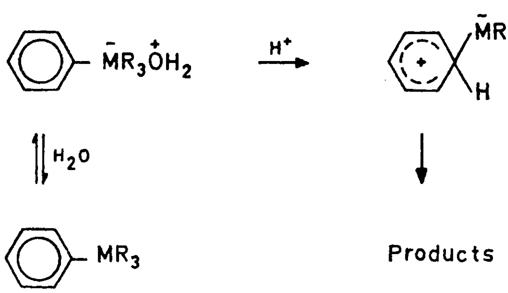
taneously to offer evidence that the dual-mechanism hypothesis proposed[2] to explain the seemingly anomalous reactivities of R_3MPh (M = C, Si, Ge, Sn, Pb) in protodemetallation reactions is unnecessary.

The Table shows the relative reactivities (k_{rel}) of Et_3MPh toward aqueous, alcoholic perchloric acid, equation (1), deduced by Eaborn and Pande.[2]

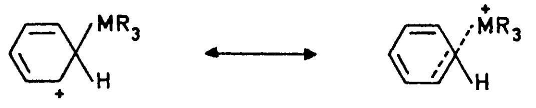
It was assumed that the basicity of the phenyl ring, and therefore the inductive effect of MR_3, would govern the rate of reaction, but the deduced rates were inconsistent with the electronegativity of R_3M.[3] The high reactivity of the tin and lead compounds was ascribed to possible solvent co-ordination with the metal prior to the rate-limiting proton attack, equation (2), whereas the remaining compounds reacted *via* the accepted mechanism (1).



(1)



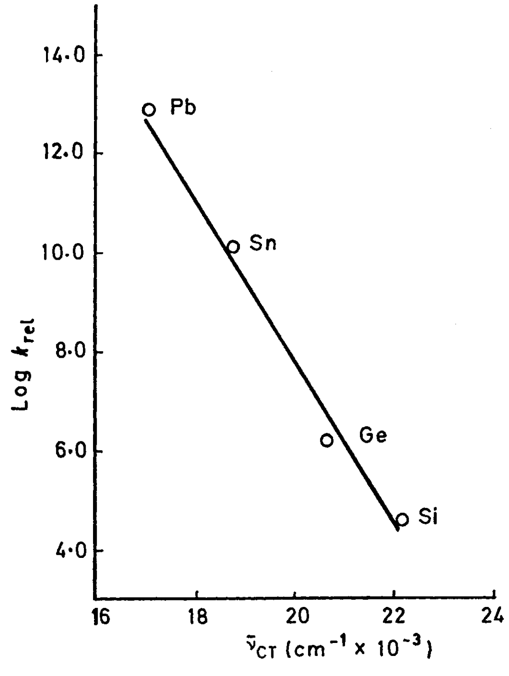
(2)



(I)

However, the intermediate in (1) can also be written as the cation (I) and the stability of such ions is known to increase greatly as one varies M down the series from carbon to lead. Traylor, *et al.*,[4] have shown that the degree of cation stabilization by the β-metallomethyl group (R_3MCH_2–) is reflected in the energy of charge-transfer (CT) between R_3MCH_2Ph and a common π-acceptor, and that such stabilization arises from overlap of the C–M σ-bond with the empty *p*-orbital of the carbonium ion, *i.e.* resonance stabilization *via* σ–π conjugation.

The stabilization afforded a positive centre by the substituent Ph_3MCH_2- is shown as a lowering of the energy of charge transfer ($\bar{\nu}_{CT}$) between Ph_3MCH_2Ph and tetracyanoethylene (TCNE); the magnitude is evident from the σ^+_{CT} values for the substituent (see Table). A plot of ν_{CT} against log k_{rel} yields a linear relationship (Figure), indicating that whatever factors influence the variation of $\bar{\nu}_{CT}$ with respect to M also influence log k_{rel}. If one considers the R_3MCH- moiety in (I) as a substituent on the positive centre, then approximate σ^+ values for this substituent may be calculated from k_{rel}. These values (σ^+_{calc} in the Table) show the same trend as, and similar magnitude to, the σ^+_{CT} values for the Ph_3MCH_2 substituent; [σ^+_{CT}(Me_3SiCH_2) = − 0·6 and σ^+_{CT}(Me_3SnCH_2) = − 0·9].[4]



FIGURE

Thus the same cation-stabilizing mechanism is operative in both the CT complexes and the protodemetallation intermediates, *viz.* σ–π conjugation by the carbon–metal bond,[4,5] and the relative rates for protodemetallation of Et_3MPh properly reflect the increasing stabilization of the reaction transition state as one varies M down the column of Group IV elements.

Thus it is the substituent being displaced which governs the rate of the reaction, an *ipso* effect capable of changing the reaction rate by a factor of 10^{13}.

(*Received*, 13*th December* 1971; *Com.* 2118.)

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[1] C. L. Perrin and G. A. Skinner, *J. Amer. Chem. Soc.*, 1971, **93**, 3389.

[2] C. Eaborn and K. C. Pande, *J. Chem. Soc.*, 1970, 1566.

[3] Electronegativities were those of A. L. Allred and E. G. Rochow, *J. Inorg. Nuclear Chem.*, 1958, **5**, 269.

[4] W. G. Hanstein, H. J. Berwin, and T. G. Traylor, *J. Amer. Chem. Soc.*, 1970, **92**, 829.

[5] T. G. Traylor, W. G. Hanstein, and H. J. Berwin, *J. Amer. Chem. Soc.*, 1970, **92**, 7476.

[6] C. Eaborn, *J. Chem. Soc.*, 1956, 4858.