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SPECTROSCOPIC EVIDENCE FOR THE REDUCTION OF ALKYL HALIDES BY METAL HYDRIDES VIA A SINGLE ELECTRON TRANSFER MECHANISM

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Summary: This report provides spectroscopic evidence to support a single electron transfer pathway to describe the reaction of metal hydrides with alkyl halides by direct EPR observation of the radical formed in the reaction.

Main-group metal hydrides have been extensively used as reducing agents for a wide variety of organic substrates. In general, these hydrides have been thought to react as nucleophilic reagents in transferring a hydride ion to substrates such as organic halides.[1] Recently we reported that reactions of various main-group metal hydrides with dimesitylketone,[2] polynuclear hydrocarbons[3] and alkyl halides[4] proceed mechanistically via a single electron transfer (SET) pathway. The evidence for the proposed SET pathway in these reactions was based on direct visible and EPR spectroscopy (e.g., in the case of reactions of metal hydrides with dimesitylketone and polynuclear hydrocarbons) or indirectly by product formation studies (e.g., in the case of reactions of metal hydrides with alkyl halides) using cyclizable probes. In order to support the proposed SET pathway for the reactions of metal hydrides with alkyl halides, we decided to study, by EPR spectroscopy, those reactions that might produce stable radical intermediates. Here we report such studies involving the reactions of metal hydrides with trityl halides.

Various simple and complex metal hydrides such as AlH_3, MgH_2, HMgCl, HMgBr, B_2H_6, $LiAlH_4$ and $NaAlH_4$ were allowed to react with trityl halides (Ph_3CX; where X = Cl or Br) in tetrahydrofuran.

$$Ph_3CX + MH \longrightarrow Ph_3CH + MX \qquad (1)$$

These reactions proceeded rapidly and a yellow color developed immediately in the case of HMgBr, HMgCl and MgH_2. In the case of AlH_3 the color was yellow with a slight orange tint and in the case of $LiAlH_4$ the color was yellow-orange. In each case the color increased in intensity with time and then slowly faded. The reaction solutions were found to be EPR active and showed an EPR spectrum (Fig. 1) in each case consistent with that of the trityl radical,[5] $Ph_3\dot{C}$. This signal was not present in the EPR spectra of the trityl halides. The intensity of the signal increased rapidly with time and reached a maximum (estimated intensity ≃ 6-14%) beyond which it slowly decreased (Fig. 2).[6]

The rate of radical formation as well as its decay was found to be dependent on the nature of the particular metal hydride employed. The reduction product of these reactions is triphenylmethane (Ph_3CH) which is continuously formed during the course of the reaction (Fig. 1) and whose rate of formation is also dependent on the nature of a particular metal hydride employed. In order to determine the extent of H-atom abstraction by the trityl radical from either the metal hydride radical-cation or the solvent, similar experiments were carried out using metal deuterides. In

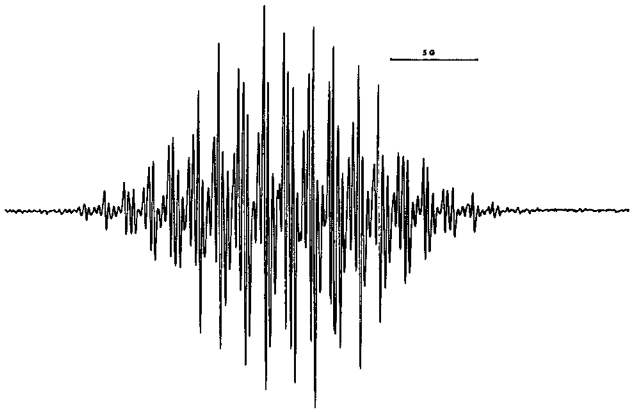

Figure 1: EPR spectrum of the trityl radical intermediate formed in the reactions of trityl halides with metal hydrides in THF at room temperature.

each case, a high yield of deuterium incorporation product, Ph_3CD (>90%) was obtained suggesting that hydrogen is abstracted predominantly from the metal hydride radical-cation intermediate. A mechanism (Scheme 1) is proposed for these reactions.

SCHEME 1

$$Ph_3CBr + M\text{-}D \longrightarrow [(Ph_3CBr)^{\dot{-}}(M\text{-}D)^{\dot{+}}] \longrightarrow [Ph_3C\cdot + Br^- + (M\text{-}D)^{\dot{+}}]$$

(Solvent Cage)

$$[\ldots] \longrightarrow Ph_3CD + M\text{-}Br; \quad Ph_3CD \xrightarrow[-D_2]{MD} Ph_3CM \xrightarrow{H_2O} Ph_3CH$$

$$[\ldots] \xrightarrow{SH} Ph_3CH$$

This proposed pathway suggests that, on mixing the two reactants, one electron is transferred from the metal hydride (deuteride) to the trityl halide which subsequently produces the trityl radical. The concentration of the radical is dependent on the ease of hydrogen (deuterium) transfer from the metal hydride radical-cation which is related to the reactivity of the metal hydride. Indeed, the product Ph_3CH (or Ph_3CD) is formed much more rapidly from $LiAlH_4$ or $NaAlH_4$ compared to HMgBr or AlH_3. Again, the amount of deuterium incorporation (when M-D is employed) is dependent on the reactivity of the metal hydride. Thus, high deuterium incorporation product (Ph_3CD = 90%) is observed in the reaction of $LiAlD_4$ with Ph_3CBr and (Ph_3CD = 96%) in the reaction of DMgBr with Ph_3CBr. The small amount of Ph_3CH formed in this reaction can be explained either by abstraction of hydrogen from the solvent or an alternative route involving a further reaction of Ph_3CD with MD, resulting in the formation of Ph_3CM which upon hydrolysis forms Ph_3CH. Indeed, a slow gas evolution (H_2 or D_2) was observed when the above reaction mixture was allowed to stand for a long period of time and the amount of deuterium incorporation product decreased with time. Surprisingly in this reaction, formation of a small amount (< 1%) of $Ph_3C\cdot$ was observed which can be explained by the following reaction sequence (eqs. 2,3).[8]

$$Ph_3CH + MH \longrightarrow Ph_3C^- + M^+ + H_2 \quad (1)$$

$$Ph_3C^- + Ph_3CH \longrightarrow 2Ph_3C\cdot + H\cdot \quad (2)$$

Additionally, the orange color in these reaction mixtures involving more reactive hydrides ($LiAlH_4$,

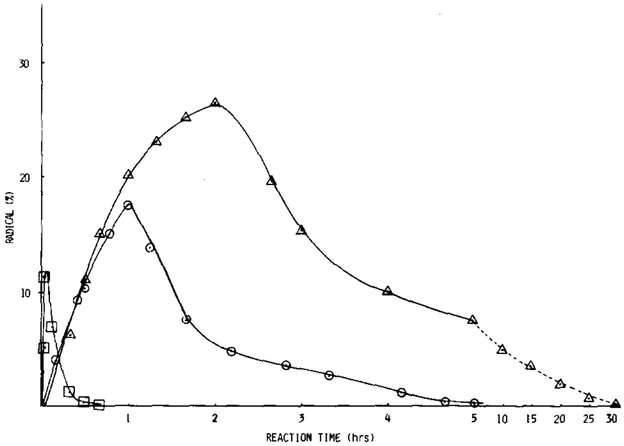

Figure 2: Formation of the trityl radical with time determined by EPR spectroscopy in the reaction of trityl bromide with metal hydrides. (A) □ -$LiAlH_4$, (B) O -AlH_3, (C) Δ -HMgBr.

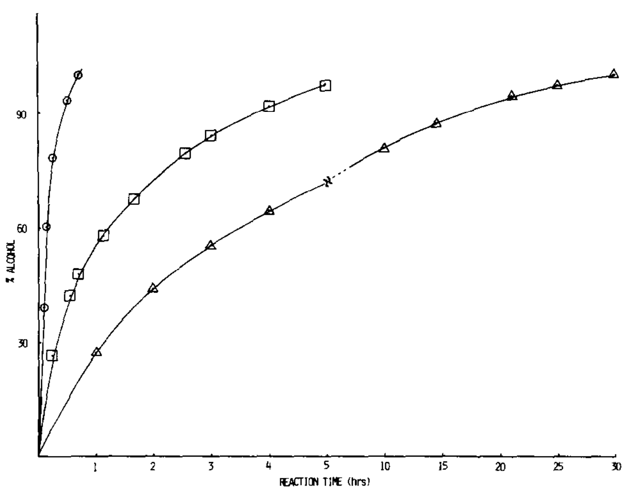

Figure 3: Formation of the reduction product (Ph_3CH) with time determined by GLC in the reaction of trityl bromide with metal hydrides. (A) O -$LiAlH_4$, (B) □ -AlH_3, (C) Δ -HMgBr.

AlH_3) can be explained by the fact that one would expect the reaction of product (Ph_3CH) with MH to form Ph_3CM more readily as the reactivity of the metal hydride increases. This is consistent with what we observed (color formation, Ph_3C^- is red in solution) namely, the reaction of $LiAlH_4$ with Ph_3CBr produces some Ph_3C^- as evidenced by the orange-red color of the reacting solution.[9]

This study does not imply that all alkyl halides are reduced by metal hydrides via a SET process, however, it does imply that at least in the cases where stable radicals can be formed that such a pathway is in effect. Work is in progress to establish the importance of the nature of the alkyl halide in determining the scope of the SET pathway in alkyl reductions by metal hydrides.[10]

REFERENCES

1. L.W. Trevoy and W.G. Brown, J. Amer. Chem. Soc., 71, 1675 (1949); H.O. House, Modern Synthetic Reactions, 2nd. Ed., W.A. Benjamin, Menlo Park, CA (1972); H.C. Brown and S. Krishnamurthy, J. Org. Chem., 45, 849 (1980).
2. E.C. Ashby, A.B. Goel and R.N. DePriest, J. Amer. Chem. Soc., 102, 7779 (1980).
3. E.C. Ashby, A.B. Goel, R.N. DePriest and H.S. Prasad, J. Amer. Chem. Soc., 103, 973 (1981).
4. E.C. Ashby, R.N. DePriest and A.B. Goel, Tetrahedron Lett., (In Press).
5. F.C. Adam and S.I. Wiesman, J. Amer. Chem. Soc., 80 2057 (1958).
6. Radical concentrations were determined by EPR spectroscopy using the one-modulation technique.[7] The estimated intensity of the trityl radical (≃6-14%) was based on the initial concentration of Ph3CX.
7. M. Okubo, Bull. Chem. Soc., Japan, 218 2057 (1975).
8. H.E. Zieger, J. Angres and L. Maresca., J.Amer. Chem. Soc., 95, 8203 (1973).
9. In order to eliminate the possiblility of a photochemically induced radical generation, the reactions of Ph_3CX with metal hydrides were also carried out in the dark. Radical intermediates were readily observed in the dark as well.

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