

Figure 1. Brønsted plot for proton transfer from the conjugate acid of 2,7-dimethoxy-1,8-bis(dimethylamino)naphthalene to external bases in aqueous solution at 25 °C. The oxygen bases (open circles) are, from left to right, $\text{CF}_3\text{CH}_2\text{O}^-$, CH_3CHNO^- , $\text{C}_6\text{H}_5\text{CHNO}^-$, 3,4- $(\text{CH}_3)_2\text{C}_6\text{H}_3\text{O}^-$, $\text{C}_6\text{H}_5\text{O}^-$, 4- $\text{ClC}_6\text{H}_4\text{O}^-$, 2- $\text{ClC}_6\text{H}_4\text{O}^-$, 2,4- $\text{Cl}_2\text{C}_6\text{H}_3\text{O}^-$, 4- $\text{NO}_2\text{C}_6\text{H}_4\text{O}^-$, 2,4,6- $\text{Cl}_3\text{C}_6\text{H}_2\text{O}^-$, and the nitrogen bases (triangles) are, from left to right, $(\text{CH}_2)_5\text{NH}$, $\text{CH}_3\text{O}(\text{CH}_2)_3\text{NH}_2$, $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$, $(\text{CH}_3\text{O})_2\text{CHCH}_2\text{NH}_2$, $\text{CN}(\text{CH}_2)_2\text{NH}_2$, and $\text{CF}_3\text{CH}_2\text{NH}_2$.

with a sharply curving portion joining limbs of zero and unit slope, as expected for a normal acid-base reaction.¹ Nitrogen bases react more slowly than oxygen bases of the same pK_a ; part of this difference could be an electrostatic effect inasmuch as the oxygen bases are all negatively charged, but the more gradual curvature shown by the nitrogen bases indicates that these N-to-N proton transfers are also intrinsically slower than the N-to-O transfers of the other set. This is expected on the basis of the lower electronegativity and consequent poorer hydrogen-bond accepting ability of nitrogen bases.^{1,8} The hydroxide ion shows an anomalously high reactivity, which again is the expected result for a normal acid externally hydrogen bonded to solvent reacting by a Grothuss-chain mechanism.

These results are the expected behavior for the two-step reaction scheme of eq 1, and assignment of this mechanism confirms the conclusion reached in previous studies of the kinetics of protonation of 2,7-dimethoxy-1,8-bis(dimethylamino)naphthalene in Me_2SO -water solution.^{4b} The pK_a of protonated 2,7-dimethoxy-1,8-bis(dimethylamino)naphthalene has also been estimated from measurements made in Me_2SO -water solution, but the result obtained, $\text{pK}_a = 16.3$,⁵ is considerably less than the value, $\text{pK}_a = 19$ – 20 , deduced for wholly aqueous solution from the position of the break in the present Brønsted plot (Figure 1) and the lowering of the horizontal limb of this plot from the value expected for an encounter-controlled reaction.

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(8) Taft, R. W.; Gurka, D.; Joris, L.; von R. Schleyer, P.; Rakshys, J. W. *J. Am. Chem. Soc.* **1969**, *91*, 4801–4808. Pauling, L. "The Nature of the Chemical Bond"; Cornell University Press: Ithaca, NY, 1944; Chapter 9.

Metal Hydride Reductions via Single Electron Transfer. 2. Evidence for an Electron-Transfer Pathway in the Reactions of Simple and Complex Metal Hydrides of the Main Group Metals with Polynuclear Hydrocarbons

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Simple and complex metal hydrides of the main group metals are extensively used in synthetic organic chemistry as reducing

agents.¹ Generally, their reactions with organic substrates such as ketones, unsaturated hydrocarbons, alkyl halides, etc., have been considered to proceed via a polar mechanism.^{1,2}

Recently, reports from our laboratory³ as well as others⁴ have indicated the importance of single electron transfer (SET) in describing the mechanism of addition of main group organometallic compounds to ketones. More recently we have demonstrated that metal hydrides as well do indeed react with aromatic ketones via a single electron transfer mechanism.⁵ In view of our recent findings with ketones, we decided to investigate single electron transfer of metal hydrides with organic substrates more broadly in order to test the scope of our initial findings. In this connection we are attempting to detect SET either by using a probe that will indicate a SET intermediate⁶ or simply by selecting substrates whose radical intermediates formed by the electron transfer are stable enough to be studied spectroscopically. Here we wish to present evidence for the reactions of various simple and complex metal hydrides of the main group metals with polynuclear hydrocarbons via a SET mechanism as indicated by EPR and visible spectra of the intermediate radical anions.

In general, reactions of metal hydrides with organic substrates such as polynuclear hydrocarbons can be considered to involve two major steps. In the first step, the metal hydride reacts with the substrate via either SET to give a radical anion intermediate or by a polar mechanism transferring a hydride ion to the hydrocarbon. The next step of the SET or polar mechanism involves the conversion of the intermediate to the product. The present studies concentrate mainly on the first step of the reaction, and only preliminary results are presented here concerning the later stages of the reaction. To the best of our knowledge there is only one report available on the reaction of a metal hydride (LiAlH_4) with a hydrocarbon (anthracene) to give a reduction product. The reported mechanism was thought to be polar.⁷

When a simple or complex metal hydride of a main group metal [LiAlH_4 , NaAlH_4 , AlH_3 , MgH_2 and HMgCl] is allowed to react with a polynuclear hydrocarbon such as naphthalene, anthracene, phenanthrene, 2,3-benzanthracene, chrysene, benzo[*a*]pyrene, and perylene, in THF, a colored solution results. The rate of development of this color is dependent on the reactivity of the individual metal hydride, the reduction potential of the polynuclear hydrocarbon, the solvent, and the concentration of both reagents. Thus, the most reactive hydrides, LiAlH_4 and NaAlH_4 , react with perylene (reduction potential = -1.64 eV) at 10^{-4} M concentration in THF at room temperature to give a blue intermediate, the intensity of which reaches $\approx 80\%$ within 2 days [as determined by visible spectroscopy (λ_{max} 578 nm; Table I)] and increases slowly thereafter. On the other hand, naphthalene (reduction potential = -2.56 eV) produces only a trace amount of colored intermediate even at much higher concentration and after 10 days' reaction time. Similarly, the least reactive hydride reagent, HMgCl , reacts with perylene to give only about 20% intermediate after 15 days' reaction time. The colored intermediates obtained in these reactions are paramagnetic in nature and show well-resolved EPR spectra (Figure 1). The EPR and visible spectra were found to be similar to that of the radical anion, irrespective of the counterion.⁸⁻¹⁰ For example, there is no appreciable difference in the spectrum of the reaction product of perylene with LiAlH_4 or NaAlH_4 (Table II). This observation is consistent

(1) N. G. Gaylord, "Reduction with Complex Metal Hydrides", Wiley-Interscience, New York, 1956. M. N. Rerick in "Reduction", R. L. Augustine, Ed., Marcel Dekker, New York, 1968.

(2) H. O. House, "Modern Synthetic Reactions", W. A. Benjamin, Menlo Park, CA, 1972.

(3) E. C. Ashby, *Pure Appl. Chem.*, **52**, 545 (1980), and references therein.

(4) T. Holm and I. Crossland, *Acta Chem. Scand.*, **25**, 59 (1971).

(5) E. C. Ashby, A. B. Goel, and R. N. DePriest, *J. Am. Chem. Soc.*, **102**, 7779 (1980).

(6) E. C. Ashby et al., unpublished results.

(7) I. Granth, Y. Segall, H. Leader, and R. Alkabetz, *J. Org. Chem.*, **41**, 3682 (1976).

(8) T. Shida and S. Iwata, *J. Am. Chem. Soc.*, **95**, 3473 (1973).

(9) A. Carrington, F. Draunicks, and M. C. R. Symons, *J. Chem. Soc.*, 947 (1959).

(10) J. Robinson, *J. Chem. Phys.*, **53**, 4725 (1970).

Table I. Reaction of LiAlH_4 with Polynuclear Hydrocarbons in THF at 24 °C^a

hydrocarbon	molarity, 1×10^{-4} M	reaction time, days	color	radical anion ^b (approx.), %	EPR data		visible spectrum		ref
					g value	no. of lines observed	λ_{max} , nm	ϵ (1×10^{-3})	
anthracene	300	15	light blue	8	2.0029	43	657	7	8, 9
benzo[a]pyrene	1	5	violet	40	2.0031	93	521	10	8, 10
chrysene	4	7	blue-green	10	2.0035	111	470		8
2,3-benzanthracene	1	5	yellow	>50	2.0032	65	398	~60	8, 9
phenanthrene	4	7	blue	9	2.0030	43	358	13.8	8
perylene	1	2	blue	80	2.0029	59	459	63	8, 9
naphthalene	500	10		trace	2.0030	11	577		16

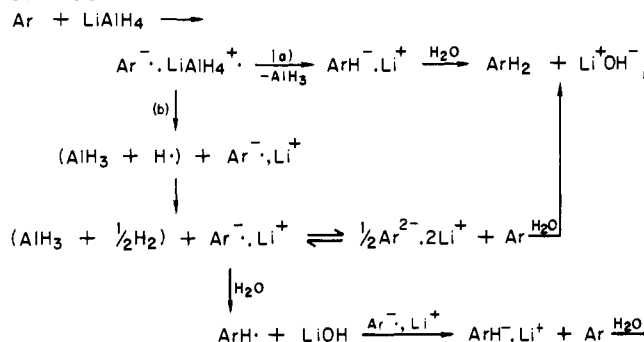
^a Hydride reagent was used in fivefold excess. ^b The amount of radical intermediate increases steadily with time and the percentage of radical-anion intermediate was calculated at the given time from the values of the extinction coefficient as well as by integrating the EPR spectra. Values are within $\pm 5\%$ of the reported values.

Table II. Reaction of Perylene with Metal Hydrides in THF at 24 °C^a

hydride	molarity of hydrocarbon, 1×10^{-4} M	reaction time, days	color	radical anion (approx.), ^b %	EPR data ^{17,9}		visible spectrum
					g value	no. of lines observed	λ_{max} , nm
LiAlH_4	1	2	blue	80	2.0029	59	577
NaAlH_4	1	2	blue	80	2.0029	59	578
AlH_3	1	5	blue	31	2.0030	59	578
MgH_2	1	7	blue	35	2.0030	59	578
HMgCl	1	15	blue	20	2.0029	59	578

^a Hydride reagents were used in fivefold excess. ^b Percentage of radical anion was determined by comparing with perylene negative ion, $\epsilon = 63\,000$, in the visible and by EPR signal integration. Values are within $\pm 5\%$ approximation.

Scheme I



with the existence of the radical anion as a solvent-separated ion pair.

The rates of the SET reactions between metal hydride and hydrocarbon are slow and can be accelerated by using an excess of metal hydride. However, in some cases when a large excess of hydride is used, formation of the dianion takes place as a consequence of additional electron transfer to the monoanion. Reduction to the dianion is again dependent on the reduction potential of the hydrocarbon;¹¹ e.g., in the case of anthracene (reduction potential = -1.96 eV), no appreciable dianion formation was observed even when a 10-fold excess of LiAlH_4 was used.

Thus, it appears from the EPR and visible spectroscopic studies on the intermediates produced in these reactions that a single electron is being transferred from the metal hydride to the hydrocarbon forming a radical-anion-radical-cation pair ($\text{Ar}^{\cdot-} \cdot \text{MH}^{\cdot+}$) which can either give the reduction product, $\text{ArH}^{\cdot-} \cdot \text{M}^+$, by hydrogen transfer or can generate the solvent separated ion pair, $\text{Ar}^{\cdot-} \cdot \text{M}^+$, by dissociation (Scheme I). Hydrolysis of this later intermediate can produce the reduction product via either a dianion as reported earlier in the case of perylene radical-anion protonation or via its reaction with H_2O followed by attack of another radical-anion as demonstrated (Scheme I) in the case of anthracene protonation.¹¹⁻¹⁴ In a typical reaction of anthracene with LiAlH_4

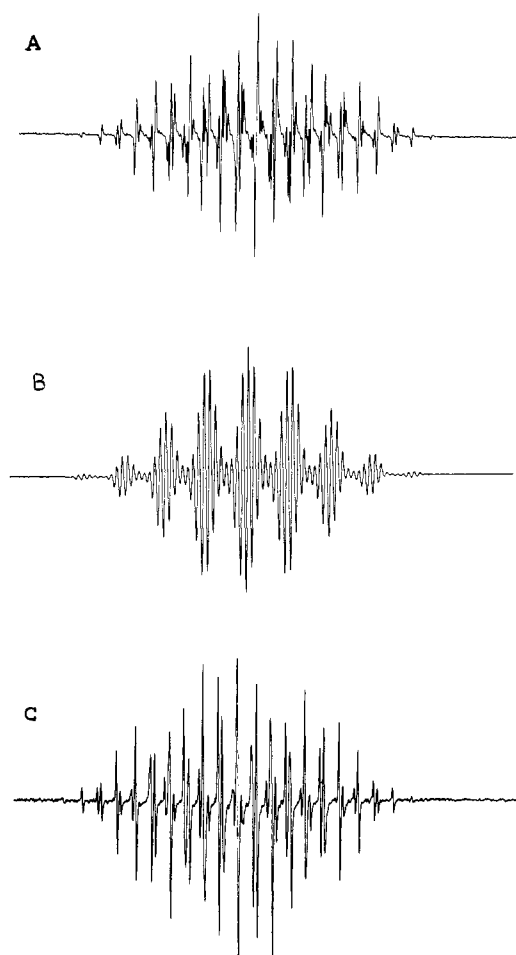


Figure 1. EPR spectrum of the reaction of (A) LiAlH_4 with anthracene, (B) LiAlH_4 with perylene, and (C) NaAlH_4 with phenanthrene in THF at room temperature (25 °C). Scale: 3.57 G/cm.

(11) S. Jensen and V. D. Parker, *J. Am. Chem. Soc.*, **97**, 5211 (1975).

in THF, slow hydrogen gas evolution takes place continuously over the reaction period. Upon hydrolysis of the intermediate reduction products, 9,10-dihydroanthracene, (ArH₂ when hydrolyzed with H₂O) and 9,10-dihydroanthracene-9-d (ArHD and ArD₂ when hydrolyzed with D₂O) are obtained. On the other hand, when the above reaction is carried out by using LiAlD₄ under the identical reaction conditions, hydrolysis with H₂O again produced both ArHD and ArH₂. These results indicate the presence of a solvent-separated ion pair (Ar⁻,M⁺ as well as ArH⁻M⁺ or ArD⁻M⁺) prior to hydrolysis. In the reaction with LiAlH₄ more ArHD is formed than ArH₂ (when hydrolyzed with D₂O), and in the reaction with LiAlD₄ more ArH₂ is formed than ArHD (when hydrolyzed with H₂O), indicating that more of the reaction is proceeding via pathway b than pathway a. The mechanism of hydrolysis had been studied earlier by previous workers; however, we are actively studying the later part of the reaction.

(12) G. Levin, C. Sutphen, and M. Szwarc, *J. Am. Chem. Soc.*, **94**, 2652 (1972).

(13) A. Rainis, S. Tung, and M. Szwarc, *J. Am. Chem. Soc.*, **95**, 659 (1973).

(14) A. Rainis and M. Szwarc, *J. Am. Chem. Soc.*, **96**, 3008 (1974).

(15) We are grateful for support of this work by the National Science Foundation (Grant No. MPS 7504127).

(16) H. M. Assenheim, "Introduction to Electron Spin Resonance", Hilger and Watts Ltd, London, 1966, pp 115-118.

(17) E. de Boer and S. I. Weissman, *J. Am. Chem. Soc.*, **80**, 4549 (1958).

Photogeneration of Very Active Homogeneous Catalysts Using Laser Light Excitation of Iron Carbonyl Precursors

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Photoinitiation of homogeneous catalysis by irradiation of thermally inert iron carbonyl catalyst precursors has been demonstrated to be a procedure for effecting olefin isomerization, hydrogenation, and hydrosilation reactions at low temperature¹⁻³ compared to thermal catalysis.⁴ However, there has been very little quantitative information concerning the activity of photogenerated catalysts. In this communication we wish to report preliminary experiments that show that Fe(CO)₅ and Fe₃(CO)₁₂ are photochemical precursors to thermally active catalysts that rival the fastest homogeneous catalysts known.⁵ The catalytic chemistry studied has been that represented by eq 1 and 2 and the question addressed has been what is the turnover rate for the photogenerated catalysts? Answering such a question is important in establishing whether photoinitiation of catalysis can provide products at a useful rate. But the answer is not straightforwardly obtained, since the actual catalyst in this system is not well characterized. We have taken an approach that allows us to put some lower limits on the activity of the catalyst.

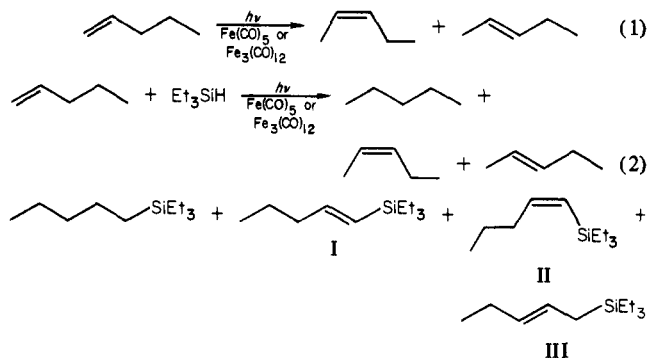
(1) Schroeder, M. A.; Wrighton, M. S. *J. Am. Chem. Soc.* **1976**, *98*, 551; *J. Organomet. Chem.* **1977**, *128*, 345.

(2) (a) Asinger, F. Y.; Fell, B.; Schrage, K. *Chem. Ber.* **1965**, *98*, 372, 381. (b) Asinger, F.; Fell, B.; Collin, G. *Ibid.* **1963**, *96*, 716. (c) Carr, M. D.; Kane, V. V.; Whiting, M. C. *Proc. Chem. Soc., London* **1964**, 408.

(3) Austin, R. G.; Paonessa, R. S.; Giordano, P. J.; Wrighton, M. S. *Adv. Chem. Ser.* **1978**, No. 168, 189.

(4) (a) Howard, J. F.; Chalk, A. J. *Org. Synth. Met. Carbonyls* **1977**, *2*, 680-694. (b) Frankel, E. N.; Emken, E. A.; Peters, H. M.; Davison, V. L.; Butterfield, R. O. *J. Org. Chem.* **1964**, *29*, 3292, 3620.

(5) (a) James, B. R. "Homogeneous Hydrogenation"; Wiley: New York, 1973. (b) Taqui Khan, M. M.; Martell, A. E. "Homogeneous Catalysis by Metal Complexes"; Academic Press: New York, 1974; Vol. I and II and references therein.



The observed quantum yield for consumption of 1-pentene according to (1) or (2) significantly exceeds unity¹⁻³ and indicates that an active catalyst is generated photochemically. But the quantum yield at a single light intensity only gives the efficiency for utilizing incident quanta. The quantum yields from Fe(CO)₅ or Fe₃(CO)₁₂ photocatalyzed reactions are not found to be infinite; catalysis does not persist in the dark after photoinitiation in these systems. Sealed reaction vessels lead to the possibility of the catalyst back reacting with photoejected CO while purging with an inert gas to remove the CO leads to clusters that are catalytically inactive. This chemistry complicates the determination of catalyst turnover rate. Thus, the approach we have taken has been to determine the observed rate of 1-pentene consumption by using very high light intensity excitation where the catalyst turnover rate, not photogeneration of the catalyst, could become the rate-limiting feature. The results are given below.

Photocatalysis experiments according to eq 1 and 2 were carried out by using an Ar ion laser as the excitation source to provide very high light intensity. Consumption of 1-pentene as a function of irradiation time proves to be a very fast process. Typically, we have monitored the chemistry by gas chromatography, but in these experiments we found that the reaction is so fast that we became concerned about the finite time interval involved in opening hermetically sealed ampules to quench any residual dark catalytic activity.

Irradiation of several samples for equal time followed by analysis of each at a different time after irradiation reveals no dark aftereffects; that is, it would appear that when the light is turned off catalysis ceases essentially instantly. The time resolution of this sort of experiment is <30 s, the time needed to quench any catalytic activity by exposing the solutions to O₂ by opening the hermetically sealed ampules. We have found that neat 1-pentene solutions can be quantitatively analyzed by near-infrared absorption spectroscopy. Figure 1 shows the results of catalysis on a portion of the near-infrared spectrum of 1-pentene. Independent measurement of the spectra of pure *cis*-2-pentene and pure *trans*-2-pentene in the same wavelength range shows that the spectral changes shown in Figure 1 are consistent with the chemistry represented by eq 1 where the ratio of *trans*-2-pentene to *cis*-2-pentene is roughly 3:1. The near-infrared spectrum of 1-pentene shows bands not present in the 2-pentenenes and allows quantitative analysis of 1-pentene disappearance on a time scale much faster than gas chromatography. Comparison of a near-infrared spectrophotometric analysis and gas chromatographic analysis of 1-pentene disappearance shows that the near-infrared is a reliable quantitative technique. Monitoring the unique near-infrared absorbance of 1-pentene shows that catalysis persists for <5 s after irradiation of Fe(CO)₅/1-pentene mixtures is terminated. Flash photolysis followed by monitoring at 1330 nm shows that catalysis is over within a few seconds after the light is switched off (vide infra).

Table I summarizes typical data for photocatalysis experiments using high light intensity continuous laser excitation. The shortest convenient irradiation time was 5 s in such experiments, and roughly 25-50% conversion of neat starting material to product could be obtained by using either Fe(CO)₅ or Fe₃(CO)₁₂. In the reaction of HSiEt₃ with 1-pentene, the 2-pentenenes account for only ~25% of the 1-pentene reacted; that is, 75% of the 1-pentene