

Table I. Results for Nitron Spin Traps

spin trap	rate constants, M ⁻¹ s ⁻¹	oxygen evolu- tion ratio ¹¹	spin adduct formation
PBN	1.4 × 10 ⁸	0.33	none
4-PyBN	1.4 × 10 ⁸	0.30	none
4-PyOBN	1.2 × 10 ⁸	0.32	<10 ⁻⁷ M a ^N = 15.0 G; a _β ^H = 1.7 G
4-MePyBN	8.0 × 10 ⁷	0.30	<5 × 10 ⁻⁷ a ^N = 14.8 G; a _β ^H = 1.5 G
2-SSPB	9.4 × 10 ⁷	0.30	none
DMPO	1.8 × 10 ⁷		<10 ⁻⁷ M a ^N = 14.9 G; a _β ^H = 14.9 G

quenching, K_Q , and for the reaction of 1O_2 with PBN, K_A .⁸ K_Q was determined to be $1.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, which can be compared to the literature value of $2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.⁹ K_A was found to be $1.4 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. Hence these quenching experiments confirm that PBN does undergo a chemical reaction with 1O_2 in water. No comparatively significant reaction occurred between methylene blue and PBN in the absence of oxygen or between methylene blue and N_3^- in the presence of oxygen upon illumination.

Table I lists the various nitrones which we have now studied.¹⁰ The rate constants were obtained by measuring the relative rates under identical conditions and using the above-determined value of K_A for PBN. The spin trap DMPO gives a K_A almost 1 order of magnitude less than PBN. Thus, in selecting a nitron for use as a "spin trap" for ESR studies in systems thought to contain 1O_2 , DMPO would be a better choice.

It is also important to know whether the product of a 1O_2 and nitron reaction leads to radical adducts, as this could lead to false conclusions in experiments whose objectives are the identification of radical intermediates. Moreover, it could lead to a diagnostic test for 1O_2 if a certain radical adduct is formed. Our experiments show, in fact, that extremely small quantities of spin adducts are generated with certain traps, whereas others lead to no observable adducts (Table I). In those cases where radical adducts were observed, the radical concentrations were 3 orders of magnitude less than the concentrations of either O_2 or PBN consumed. Nevertheless, the high sensitivity of ESR allows detection in these cases and misinterpretation is possible. For this reason, the splitting constants for the adducts where observed are also given in Table I. These splittings correspond to the $\cdot OH$ adduct of each of the spin traps.^{11,12,13} Therefore, formation of the $\cdot OH$ adduct at very low concentrations could reflect 1O_2 generation rather than $\cdot OH$ production. The ESR experiments used $1 \times 10^{-4} \text{ M}$ methylene blue and $1 \times 10^{-2} \text{ M}$ spin trap under illumination conditions similar to those for the uptake results.

The reaction product of 1O_2 with nitrones is unknown. However, addition of catalase to the system after illumination resulted in the evolution of O_2 and accounts for 30% of the oxygen consumed. Optical studies revealed that 7.8% PBN was consumed (monitoring decay at λ 290 nm) whereas the calculated percentage loss should have been 14%, using the measured oxygen uptake determined for the same sample. Since the product may have absorbance at this wavelength, a value of less than 14% would be expected.

This study reveals that nitron spin traps do react chemically with 1O_2 with a significant rate (K_A for PBN = $1.4 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) and lead to predominantly diamagnetic product(s). The technique of oxygen uptake offers a method of continuous monitoring of the chemical reactions of 1O_2 in aqueous medium. The

use of this same probe for pigment photochemistry in nonaqueous systems¹⁴ suggests that this technique could be extended to virtually all solvent systems. Clearly, nitron spin traps can be used (in conjunction with both ESR and O_2 uptake) for the detection of $\cdot OH$, O_2^- and 1O_2 in water. However, experimenters should be aware of the problems which can arise. In particular, if 1O_2 is simultaneously being produced in the systems, a rapid depletion of dissolved O_2 can occur and this may prevent a normal radical reaction which would have prevailed if the trap were absent.

(14) Harbour, J. R.; Issler, S. L.; Tromp, J.; Hair, M. L. Presented at the 179th National Meeting of the American Chemical Society, Houston, Texas, March 23-28, 1980.

John R. Harbour,* Sandra L. Issler, Michael L. Hair
Xerox Research Centre of Canada
2480 Dunwin Drive
Mississauga, Ontario L5L1J9, Canada
Received May 28, 1980

Evidence for an Electron-Transfer Mechanism in the Reduction of Ketones by Main-Group Metal Hydrides

Sir:

The reduction of ketones by hydrogen transfer from main-group metal hydrides is one of the most widely used synthetic methods in organic chemistry.¹ The mechanism of such hydrogen transfer is generally considered to be of a polar nature.^{2,3} Recent reports from our laboratory and others have shown the importance of electron-transfer (ET) mechanisms in describing the alkylation of ketones by main-group organometallic compounds. In view of our results showing that magnesium alkyls react with ketones by an electron-transfer process,⁴ we decided to study the reactions of ketones with main-group metal hydrides in order to determine if hydrogen is transferred in a manner similar to the alkyl groups when metal hydrides are allowed to react with ketones.

The kind of probe used to detect an electron-transfer process in the reaction of main-group metal alkyls with ketones involves cyclization⁴ or isomerization of the intermediate alkyl radical (A)⁵ or isomerization of a radical anion (B)⁶ (eq 1). Since it is not possible to have H \cdot as a probe in cases involving the reactions of metal hydrides with ketones, the intermediate ketyl itself has been used as the probe (eq 2).

Normally k_2 is much greater than k_1 such that detection of the intermediate ketyl would not be possible; however, if sterically hindered ketones are employed, the electron-transfer step (k_1) should not be significantly affected, yet k_2 should be greatly decreased. Of course, the hope is that k_2 can be made to be less than k_1 , in which case the ketyl could be observed spectroscopically and its disappearance with time recorded. Here we present the results of our studies, which clearly demonstrate the involvement of an electron-transfer mechanism in the reduction of ketones by main-group metal hydrides.

In the present studies, we have found that deep colored solutions are formed when dimethyl ketone (DMK) and metal hydrides such as AlH_3 , BH_3 , MgH_2 , $HMgX$ (where X = Cl or Br) are allowed to react in THF. These highly colored solutions are EPR active, suggesting them to be paramagnetic in nature. In particular, when an equimolar amount of AlH_3 ⁷ and DMK are mixed

(8) Foote, C. S., ref 7, pp 139-71.

(9) Gupta, A. K.; Rohatgi-Mukherjee, K. K. *Photochem. Photobiol.* **1978**, *27*, 539-43.

(10) These nitron spin traps were obtained from Spin Trap Producers, Guelph, Ontario N1H 6L8, Canada.

(11) These values result from the ratio of the $[O_2]$ evolved by addition of catalase to the $[O_2]$ which is consumed.

(12) Janzen, E. G.; Dudley, R. L.; Shetty, R. V. *J. Am. Chem. Soc.* **1979**, *101*, 243-5.

(13) Janzen, E. G.; Nutter, D. E.; Davis, E. R.; Blackburn, B. J.; Poyer, J. L.; McCay, P. B. *Can. J. Chem.* **1978**, *56*, 2237-42.

(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.

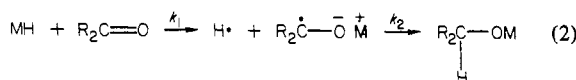
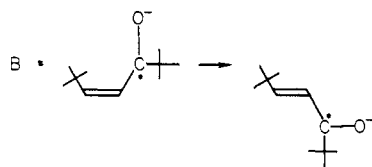
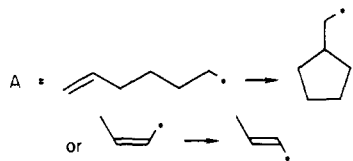
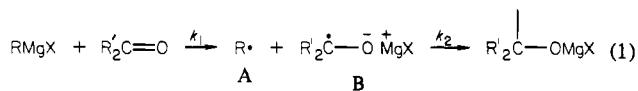
(2) H. O. House, "Modern Synthetic Reactions", W. A. Benjamin, Menlo Park, Calif., 1972.

(3) D. C. Ayres, D. N. Kirk, and R. Sawdaye, *J. Chem. Soc.*, 1133 (1970).

(4) E. C. Ashby, *Pure Appl. Chem.*, **52**, 545 (1980).

(5) E. C. Ashby and J. S. Bowers, Jr., *J. Am. Chem. Soc.*, **99**, 8504 (1977).

(6) E. C. Ashby and T. L. Wiesmann, *J. Am. Chem. Soc.*, **100**, 3101 (1978).



in THF, a violet color (λ_{max} 579 nm) appears within a few minutes. This colored solution shows a complex EPR signal (Figure 1). The spectrum consists of several well-resolved peaks associated with a broad peak (or peaks), irrespective of the solution concentration (spectra were recorded for samples at 10^{-4} – 10^{-2} M concentration). This behavior of the spectrum is probably due to the overlapping signals of radical anion and radical cation since no other signal could be observed in the region ($g = 2.003 \pm 4000$ G).

Both the intensity of the EPR signal and the visible absorption increase and reach a maximum, beyond which decay proceeds in a first-order fashion over a period of 3 days. By UV-vis spectroscopy it is observed that the intensity of the signal at λ_{max} 269 nm ($\epsilon \sim 12000$), due to the starting ketone, decreases rapidly as the signal due to the colored intermediate species (λ_{max} 579 nm) increases. The signal due to the ketone almost completely disappears in about 10 h for a reaction of 0.07 M concentration, indicating the irreversibility of this reaction. Beyond this time, the band due to the intermediate at 579 nm decreases in a first-order fashion at the same rate that the product is formed. Thus, an estimate of the concentration of the intermediate species can be made at any time from these results and at the maximum it has been calculated to be approximately 65%. A similar value of the concentration is obtained from the EPR calibration.⁷

The final outcome of the reaction is a 100% yield of reduction product. This reduction product is formed continuously during the entire course of reaction and arises in a first-order fashion after the EPR and visible absorption reach a maximum (Figure 2). This kinetic analysis indicates the presence of a paramagnetic intermediate on the reaction pathway for reduction. On the basis of these results, a probable mechanistic scheme (Scheme I) involving a relatively stable radical cation-radical anion pair as the intermediate is proposed. The unusually high stability of the intermediate (A) might lead one to conclude that it is the free ketyl; however, this alternate possibility can be excluded, as we have observed that the free ketyl prepared independently does not abstract hydrogen either from THF or from free metal hydride to give the reduction product. The first-order rate constant k_2 for the reaction of AlH_3 with DMK is $1.43 \times 10^{-5} \text{ s}^{-1}$ [$R(\text{correlation})$ 0.0996].

The reactions of MgH_2 and HMgX ($X = \text{Cl}$ and Br) with DMK in THF also exhibit an intense EPR signal and strong visible absorption (λ_{max} 638 and 640 nm, respectively). The EPR signal observed for the intermediate of the reaction of HMgBr with DMK is found to be similar to that of the free ketyl generated from the reaction of DMK with *t*-BuMgBr. The kinetic behavior of the EPR signal and visible absorption for the magnesium hydrides is similar to that for AlH_3 , but much slower. Again high

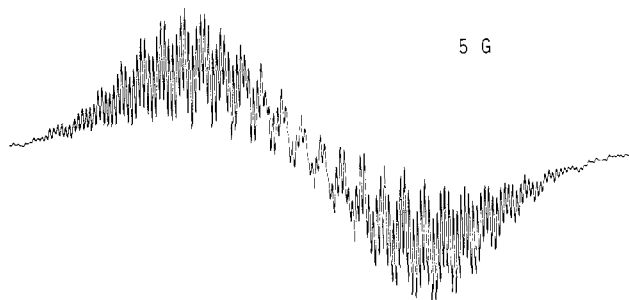


Figure 1. EPR spectrum of the reaction of AlH_3 with dimesityl ketone (0.07 M) in THF ($g = 2.0056$).

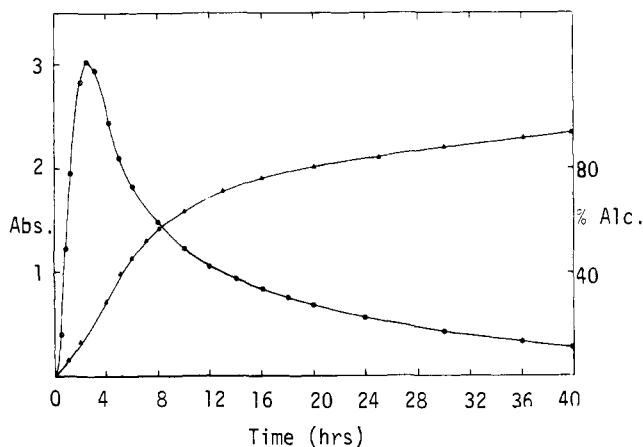
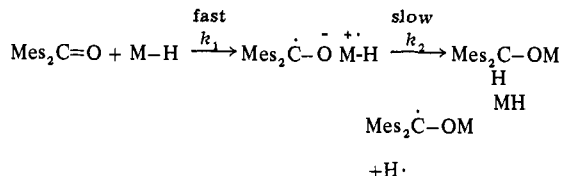


Figure 2. Reaction of AlH_3 with dimesityl ketone (0.07 M) in THF: (O) absorbance (λ_{max} 579 nm) vs. time; (Δ) product (%) vs. time (h).

Scheme I



yields of reduction product are obtained in each case. A visible absorption band (λ_{max} 638) and EPR signal is also observed for the reaction of $\text{BH}_3\cdot\text{THF}$ and DMK, although the intensities are much less.

While the steric hindrance of DMK certainly allows the observation of an intermediate by slowing down the final step (k_2), the ET mechanism should be applicable to the reaction of other less hindered but more easily reducible ketones such as benzophenone, for which no stable intermediate is observed. We are now actively pursuing further characterization of the observable ET intermediate and extending the work reported here to other substrates and complex metal hydrides.

Eugene C. Ashby,* Anil B. Goel, Robert N. DePriest

School of Chemistry
Georgia Institute of Technology
Atlanta, Georgia 30332

Received July 9, 1980

Naphthonitrile-Alkene Exciplexes. Use of Tethered Chromophores to Probe Geometric Factors in Exciplex Formation and Decay

Sir:

The aryl nitrile-olefin systems are interesting because they show exciplex fluorescence¹ as well as photoreactions. These allow

(7) AlH_3 was prepared from the reaction of LiAlH_4 with M_2SO_4 . The resulting solution was analyzed and found to be free of lithium ion.