Lewis Base Properties of Potassium-Graphite

By DAVID E. BERGBREITER* and JAMES M. KILLOUGH

(Department of Chemistry, Texas A & M University, College Station, Texas 77843)

Summary Potassium-graphite (C_8K) reacts with weak protic acids such as water and alcohols predominantly by an acid-base reaction with only small amounts of hydrogen evolution to yield a partially reduced graphite as shown by E.S.C.A. spectroscopy.

GRAPHITE forms a wide assortment of intercalation compounds in which various substrates are inserted between the planes of the carbon atoms, including those with the alkali metal such as potassium-graphite,¹ which is of interest both as a polymerization catalyst and because of its resemblence to Group 8 metals in hydrogenation, hydrogen-deuterium exchange, and Fischer-Tropsch reactions.² We describe here some details of the chemistry of potassium-graphite, namely its Lewis base character, which are relevant both to its catalytic chemistry and to its reactions as a stoicheiometric reagent. Specifically, we report that C_8K reacts with weak protic acids such as water and alcohols predominantly by proton abstraction to give a partially reduced graphite and potassium hydroxide and not by reduction leading to hydrogen evolution.

Potassium-graphite (C_8K) is easily prepared from potassium and graphite by the procedure of Lalancette.³ When water or some other proton source such as an alcohol is added to a tetrahydrofuran (THF) suspension of the gold coloured C_8K , an exothermic reaction ensues, which could be

represented by either reaction (1) or reaction (2). According to the stoicheiometry of reaction (1), 0.5 mole of

$$2C_8K + 2H_2O \rightarrow \text{graphite} + 2KOH + H_2$$
 (1)

$$C_8K + H_2O \rightarrow C_8H + KOH$$
 (2)

hydrogen will be evolved per mole of C₈K upon addition of water while none will be evolved in reaction (2). The experimental observation that addition of water leads to



FIGURE. (a) E.S.C.A. spectrum of $C_{g}K$ after reaction with water. The smaller peaks at 294 and 296 eV are due to potassium hydroxide; (b) E.S.C.A. spectrum of starting graphite.

evolution of only 0.01-0.05 mole of hydrogen per mole of $C_8 K$ or 0.01-0.08 mole of hydrogen per mole of water if an excess of water is used suggests that reaction (1) is comparatively unimportant. The predominant reaction is the simple acid-base reaction (2) leading to a partially hydrogenated graphite. In fact, the small amount of hydrogen evolution appears to be due to unchanged potassium metal from the preparation of C_8K rather than reaction (1),

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- ⁴ W. Rudorff and E. Schulze, Z. anorg. Chem., 1954, 277, 156.
- ⁵ J. F. Garst, Accounts Chem. Res., 1971, 4, 400.
- ⁶ P. Lagrange, A. Metrot, and A. Herold, Compt. rend., 1974, 278C, 701, and references therein.

although reaction (1) cannot be excluded.⁴ These results are in contrast to the known reactivity of potassium and water; they agree with the known reactivity of sodium napthalide and water.⁵ Our conclusions about the importance of reaction (2) are further supported by separate experiments which show that under our conditions (atmospheric pressure, 25 °C, THF solution), C₈K will not absorb hydrogen. Additional evidence that hydrogen is not being 'trapped' by the graphite includes the observation that the amount of hydrogen evolved rapidly reaches an equilibrium value which does not change over a 24 h period. However, C₈K does adsorb hydrogen under other conditions to form ternary graphite-potassium-hydrogen intercalation compounds.6

The product of reaction of C₈K with water in an acidbase reaction such as reaction (2) would be a reduced graphite with a disrupted aromatic system and ca. 10% hydrogen. Visual examination of this reduced graphite shows some minor physical differences such as smaller particle size, reduced lustre, and readier combustion. E.S.C.A. studies of the graphite produced reveal changes in the chemical structure from that of the starting graphite (Figure). Comparison of the carbon 1s peak of the starting graphite and of the reduced graphite shows a much broader carbon peak for the latter, indicative of the presence of more than one type of carbon atom as would be expected for a partially reduced graphite.

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