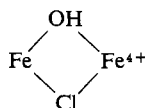


This scheme is similar to the one proposed¹³ for the formation of the chromium(III) dimer in the oxidation of $\text{Cr}_{\text{aq}}^{2+}$, except that the dissociation of the dimer is much more rapid in the iron(III) than in the chromium(III) case. The dissociation of $(\text{FeOH})_2^{4+}$ is given by

$$k_d = k_1 + k_2(\text{H}^+) \quad (5)$$

with $k_1 = 0.35 \text{ sec.}^{-1}$ and $k_2 = 3.5 \text{ M}^{-1} \text{ sec.}^{-1}$ at 25.0° . These rate constants were determined by mixing solutions containing 2.1×10^{-4} to $4.3 \times 10^{-3} \text{ M}$ iron(III) and 0.01 to 0.1 M perchloric acid with solutions containing 0.3 to 3.0 M perchloric acid, each adjusted to an ionic strength of 3.0 M with sodium perchlorate, and following the disappearance of $(\text{FeOH})_2^{4+}$ at 335 $\text{m}\mu$.

The observation that the yield of $(\text{FeOH})_2^{4+}$ in the Fe^{2+} - HOCl reactions decreases with increasing acid concentration suggests that it is perhaps formed from



The latter intermediate would tend to form the dihydroxy-bridged dimer at low acidities, while at high acidities it might tend to dissociate to Fe^{3+} (and some FeCl^{2+}). In a similar manner, the formation of FeCl^{2+} in the Fe^{2+} - Cl_2 reaction could occur in a 1-equiv. step involving chlorine atoms as intermediates, or in a 2-equiv. step involving a short-lived, dichloro-bridged dimer. These possibilities are being investigated further.

The absence of the formation of a significant amount of $(\text{FeOH})_2^{4+}$ in the Fe^{2+} - H_2O_2 reaction is of interest in view of the suggestion that this reaction involves iron(IV) as an intermediate.¹⁴

Acknowledgment. We wish to acknowledge helpful discussions with Drs. A. O. Allen and R. W. Dodson.

(13) M. Ardon and R. A. Plane, *J. Am. Chem. Soc.*, **81**, 3197 (1959).

(14) A. E. Cahill and H. Taube, *ibid.*, **74**, 2313 (1952).

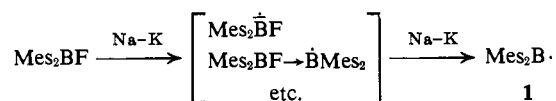
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Aryl Boron Free Radicals

Sir:

Dimesitylboron fluoride in DME (1,2-dimethoxyethane) reacts with sodium-potassium alloy to give dimesitylboron radical (1). The radical 1 is stable in degassed DME for at least 4 months, as shown by the persistence of its e.s.r. spectrum (Figure 1). If the dimesitylboron fluoride solution is not left in contact with the alloy long enough for complete conversion, the e.s.r. signal has additional lines due to intermediates.



Addition of pyridine to a DME solution of 1 produces the stable complexed radical 2 whose e.s.r. spectrum is shown in Figure 2. However, if pyridine is present in

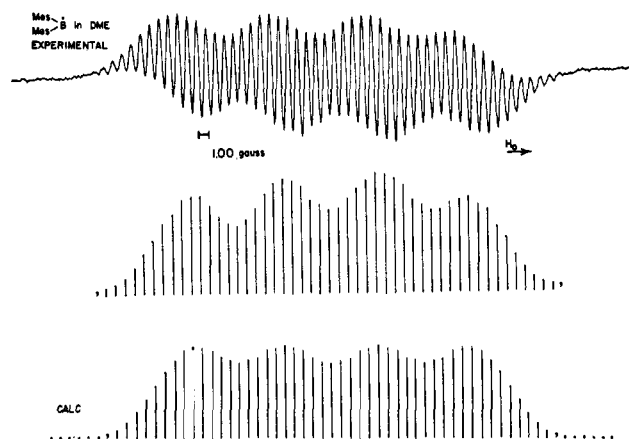


Figure 1. Observed signal and reconstructed signal of $\text{Mes}_2\dot{\text{B}}$ assuming $a_B = 10.0$ gauss, $a_H = 3.0$ gauss (*meta* hydrogens), and $a_H = 1.0$ gauss (methyl hydrogens).

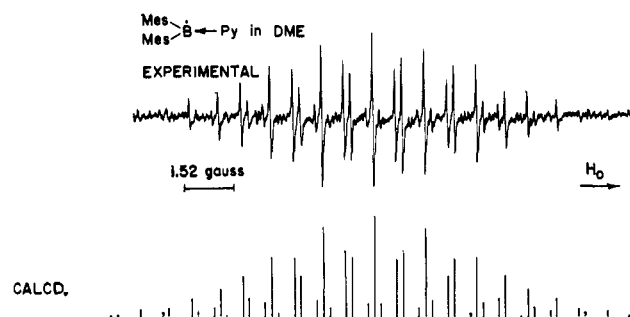
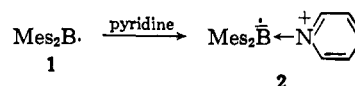


Figure 2. Observed signal and theoretical signal of $\text{Mes}_2\dot{\text{B}}\leftarrow\text{Py}$ assuming $a_B = a_N = 2.7$ gauss, $a_H = 2.7$ gauss (all five pyridine hydrogens), $a_H = 1.5$ gauss (*meta* hydrogens of the Mes groups), and $a_H = 0$ (all methyl hydrogens).

the reaction mixture initially, there is no appreciable reaction with Na-K at room temperature.¹



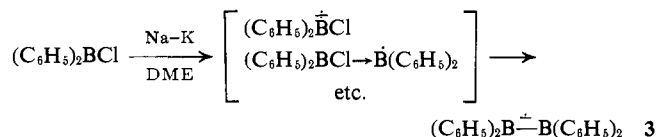
Trimesitylboron will also react with alkali metals in DME or in THF to give radicals. Reaction under mild conditions (for example, Na-Hg in THF at room temperature) gives a blue solution with four peaks with a splitting ($\Delta H_{1/2}$) of 8.0 gauss. These peaks could not be resolved into finer structures, and we believe that they are due to the trimesitylboron anion radical.² On further reaction with Na-Hg or K in THF, fine structure appears in the signal, and it becomes identical with that from the reaction of trimesitylboron with Na-K in DME or from the reaction of dimesitylboron fluoride with Na-K in DME (Figure 1).

The reaction of the less hindered diphenylboron chloride in DME with sodium-potassium alloy is more involved. An e.s.r. spectrum assigned to the radical

(1) R. Koster, G. Bertedikt, and H. W. Schrötter, *Angew. Chem.*, **76**, 649 (1964), have reported the formation of a stable radical with unresolved e.s.r. spectrum on treating diphenylboron chloride with alkali metal in the presence of pyridine in THF.

(2) S. I. Weissman, J. Townsend, D. E. Paul, and G. E. Pake, *J. Chem. Phys.*, **21**, 2227 (1953) reported that reaction with 40% Na-Hg in THF gave a quartet, but with a $\Delta H_{1/2}$ of 14 gauss. We have not observed a 14-gauss quartet in any of our experiments and have no explanation for the discrepancy at this time.

3 on the basis of hyperfine structure ($a_{B_1} = a_{B_2} = 2.1$ gauss, $a_H = 0.58$ gauss) is observed after the decay of a more complex spectrum. The spectrum assigned to 3 is succeeded in turn by one whose hyperfine structure still suggests strong interaction with two boron nuclei, but also strong interaction with a single hydrogen atom and weak interaction with only eight hydrogens. This large decrease in the number of weakly interacting hydrogens probably means that the decomposition of 3 is accompanied by the loss of two phenyl groups. A still later and final e.s.r. signal observed after further reaction with the alkali metal is the highly characteristic hyperfine spectrum of the biphenyl anion radical.^{3,4} Similar e.s.r. series terminating in the spectrum of the biphenyl anion radical are observed in experiments starting with triphenylboron or diphenylborinic anhydride in place of the diphenylboron chloride.



The cleavage of aryl groups from aryl boron is supported not only by the formation of 1 from trimesitylboron but also by the isolation of phenylboronic anhydride in some of our trapping experiments with mixtures of radicals from diphenylboron chloride. In a univalent intermediate such as phenylboron the two nonbonding electrons can occupy a low energy 2s orbital.

Acknowledgment. We are pleased to acknowledge the support of this work by the Army Research Office (Durham) and by the Atomic Energy Commission.

(3) A. Carrington and J. dos Santos-Veiga, *Mol. Phys.*, **5**, 21 (1962).

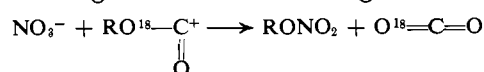
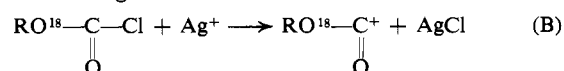
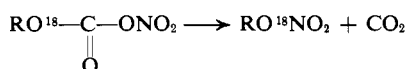
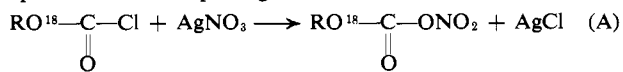
(4) It is interesting to note that the oxidation of tetraphenylborate ion also gives biphenyl, apparently by an intramolecular mechanism: D. H. Geske, *J. Phys. Chem.*, **66**, 1743 (1962).

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Reaction of Methyl Chloroformate with Silver Nitrate. A New Approach to Evidence for an Intermediate Anion in Replacement Reactions at Carbonyl Carbon

Sir:

The reaction of chloroformate esters with an acetonitrile solution of silver nitrate has been proposed as an excellent method for the synthesis of nitrate esters.^{1,2} To explain the 75% retention of the alkyl oxygen bond during a reaction of *n*-hexyl chloroformate, Boschan¹ proposed two competing mechanisms



(1) R. Boschan, *J. Am. Chem. Soc.*, **81**, 3341 (1959).

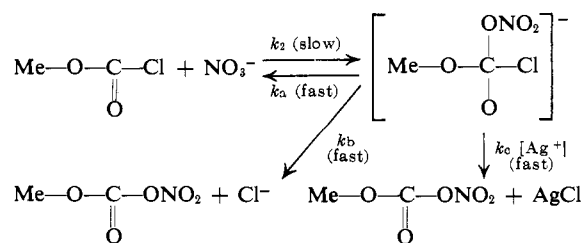
(2) G. A. Mortimer, *J. Org. Chem.*, **27**, 1876 (1962).

Under conditions for which silver nitrate reacts readily with an acetonitrile solution of methyl chloroformate, silver perchlorate showed no reaction even after 6 days. Similarly, as described below, addition of silver perchlorate to a solution of silver nitrate reacting with methyl chloroformate produced a slight retardation in rate. It is clear that direct electrophilic assistance to chloride ion removal, as proposed in reaction B, does not operate.

Reaction of methyl chloroformate with silver nitrate at 25.0°, as followed by titration of soluble silver ion, gave good second-order kinetics during at least the first 25% of reaction. The values for the second-order rate coefficient, k_2° , fell with increasing initial concentration of silver nitrate. Both the kinetics and the positions of bond fission can be rationalized by assuming that reaction always proceeds through an intermediate nitrateformate ester which then decomposes to nitrate ester by two competing mechanisms.

Boschan,¹ in proposing mechanism A, assumed that the nitrateformate ester decomposes through a four-centered transition state. However, it is attractive to consider the possibility of the nitrateformate ester decomposing through two competing ionic mechanisms. These two mechanisms can be considered to involve ionization to give ion pairs containing either nitronium ions or nitrate ions; these can then lead to nitrate ester by attack on the appropriate counterion. Such an ionization scheme would be consistent with one previously proposed by Burton and Prail³ for acyl nitrates. This aspect of the over-all scheme is currently under investigation.

The reaction scheme proposed for the formation of methyl nitrateformate can be expressed as



It follows that the observed second-order rate coefficient, k_2° , will be related to the silver nitrate concentration by the expression

$$k_2^\circ = \frac{k_2 k_b \alpha / (k_a + k_b) + [k_2 k_c \alpha^2 / (k_a + k_b)] [AgNO_3]}{1 + [k_c \alpha / (k_a + k_b)] [AgNO_3]}$$

The values for α , the degree of dissociation of silver nitrate at concentration $[AgNO_3]$, can be calculated using a value⁴ for the dissociation constant of silver nitrate of 0.015 mole/l.

The mean value of 2.00×10^{-4} l. mole⁻¹ sec.⁻¹ for the second-order rate coefficient for reaction of methyl chloroformate with 0.005 *M* to 0.04 *M* concentrations of tetraethylammonium nitrate at 25.0°, as followed by appearance of chloride ion, can be equated to $k_2 k_b / (k_a + k_b)$.

The limiting value of k_2° / α as $\alpha \rightarrow 0$, at high $[AgNO_3]$, will be k_2 . Using the experimental k_2° values, this extrapolated limit was found to be in the region of

(3) H. Burton and P. F. G. Prail, *J. Chem. Soc.*, 729 (1955).

(4) H. Strehlow and H. M. Koepf, *Z. Elektrochem.*, **63**, 373 (1958).