

from eq. 2 using  $k$  and estimates of  $B_0$ .<sup>5</sup>) To separate the dipole moment,  $\mu_{02}$ , from  $\Delta\alpha$ , the change with wave length of  $\Delta\alpha$  was estimated from the curves of Figure 1 and divided into the corresponding change in  $\Delta\alpha\mu_{02}^2$  to obtain estimates of 120 and 70 D. ( $\pm 20\%$ ) for the permanent moments of met- and oxyhemoglobin, respectively. The shape effect contribution was then estimated as about  $-40 \times 10^{-24}$  ml. for both molecules.

It is unlikely that an intrinsic anisotropy of static polarizability could lead to an orientation parallel to the short axis of the magnitude observed. If there is a mechanism favoring orientation parallel to the long axis of the molecule, such as anisotropy in a fluctuation dipole or in an ion-atmosphere polarization, the above analysis would then yield only a lower limit to the permanent dipole along the twofold axis. From this possibility it can be seen that if the data had suggested case a, no inference about the existence of a permanent dipole could have been made. Calculations of the electric dichroism suggest that no signal should have been observed for case b and the amount of orientation predicted by the Kerr effect, so that this experiment was consistent with the interpretation of the Kerr effect measurements.

It is therefore reasonable to conclude that the above experiments and analysis are evidence for a permanent dipole along the twofold axis in hemoglobin at neutral pH. The suggestion of a greater dipole moment for methemoglobin relative to oxyhemoglobin is consistent with the dielectric increment data,<sup>8</sup> although dipole moments estimated from dielectric increments (400–500 D.) apparently include contributions that are not effective in orientation, such as a randomly oriented fluctuation dipole or an ion-atmosphere polarization about an almost spherical molecule.

(8) S. Takashima, *J. Am. Chem. Soc.*, **78**, 541 (1956).

William H. Orttung

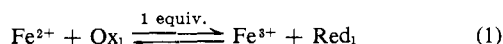
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Received October 16, 1964

## The Formation of Iron(IV) in the Oxidation of Iron(II)<sup>1</sup>

Sir:

The oxidation of  $\text{Fe}_{\text{aq}}^{2+}$  by 1-equiv. oxidants such as hexachloroiridate(IV), tris(1,10-phenanthroline)iron(III), manganese(III), and cobalt(III) proceeds in a single step. These reactions are of the type



They are generally rapid and their rates are first order with respect to the ferrous ion and the oxidant concentrations.<sup>2–4</sup> On the other hand, the oxidation of  $\text{Fe}_{\text{aq}}^{2+}$  by 2-equiv. oxidants is more complex. Such reactions have to involve unstable oxidation states of the iron or of the oxidant.

We are studying the kinetics and attempting to identify the immediate products of the reaction of  $\text{Fe}_{\text{aq}}^{2+}$  with chlorine, hypochlorous acid, hydrogen peroxide,

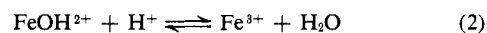
(1) Research performed under the auspices of the U. S. Atomic Energy Commission.

(2) B. M. Gordon, L. L. Williams, and N. Sutin, *J. Am. Chem. Soc.*, **83**, 2061 (1961).

(3) H. Diebler and N. Sutin, *J. Phys. Chem.*, **68**, 174 (1964).

(4) L. G. Bennet and J. C. Sheppard, *ibid.*, **66**, 1275 (1962).

and ozone. In these studies, the concentrations of  $\text{Fe}_{\text{aq}}^{2+}$  and of the oxidizing agents vary from  $10^{-4}$  to  $10^{-1}$  M and from  $5 \times 10^{-5}$  to  $5 \times 10^{-4}$  M, respectively. The perchloric acid concentration varies from 0.1 to 3.0 M. The ionic strength is 3.0 M and the temperature 25.0°. Equal volumes of two solutions containing the  $\text{Fe}_{\text{aq}}^{2+}$  and the oxidant are mixed on the flow apparatus which has been described previously,<sup>5,6</sup> and the formation of iron(III) and the dissociation of any  $\text{FeCl}^{2+}$  and  $(\text{FeOH})_2^{4+}$  produced in the reaction are followed at 240 to 280, 336, and 335 m $\mu$ , respectively.<sup>7–10</sup> Although  $\text{FeCl}^{2+}$  and  $(\text{FeOH})_2^{4+}$  have similar absorption spectra, they may readily be distinguished on the basis of their rates of dissociation. The rate of dissociation of  $(\text{FeOH})_2^{4+}$  increases with increasing acidity while the dissociation of  $\text{FeCl}^{2+}$  decreases with increasing acidity.<sup>11,12</sup> Some preliminary results of these studies are presented in Table I. Because of the rapidity of the reaction



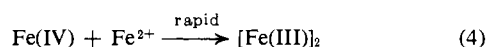
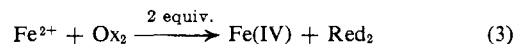
we cannot determine whether  $\text{FeOH}^{2+}$  is formed as a primary product in the oxidations.

Table I. Rate Constants and Distribution of the Products of the Oxidation of  $\text{Fe}_{\text{aq}}^{2+}$  by  $\text{H}_2\text{O}_2$ ,  $\text{Cl}_2$ ,  $\text{HOCl}$ , and  $\text{O}_3$  (Temperature 25.0°; Ionic Strength = 3.0 M)

Oxidant	$k$ , $M^{-1} \text{ sec.}^{-1}$ <sup>a</sup>	Yields, % <sup>b</sup>		
		$\text{Fe}^{3+} +$ $\text{FeOH}^{2+}$	$\text{FeCl}^{2+}$	( $\text{Fe-}$ $\text{OH})_2^{4+}$
$\text{H}_2\text{O}_2$	$65 \pm 5^c$	>99	..	<1 <sup>e</sup>
$\text{Cl}_2$	$80 \pm 5$	<30	>70 <sup>d</sup>	<5 <sup>d</sup>
$\text{HOCl}$	$(3.2 \pm 0.4) \times 10^3$	~80	$\leq 5^d$	~15 <sup>f</sup>
$\text{O}_3$	$(1.7 \pm 0.4) \times 10^5$	~60	..	~40 <sup>g</sup>

<sup>a</sup> The iron(II) was present in large excess.  $k$ , the over-all rate constant, was calculated from  $0.693/t_{1/2}[\text{Fe(II)}]$  where  $t_{1/2}$  is the half-time for the formation of iron(III). <sup>b</sup> The yields of  $\text{FeCl}^{2+}$  and  $(\text{FeOH})_2^{4+}$  are based on extinction coefficients of  $1.73 \times 10^3$  at 336 m $\mu$  and  $3 \times 10^3$  at 335 m $\mu$  for these species, respectively. <sup>c</sup> This value is in satisfactory agreement with the rate constant determined under slightly different conditions by C. F. Wells and M. A. Salam [*Nature*, **203**, 751 (1964)]. <sup>d</sup> 3.0 M  $\text{HClO}_4$ . <sup>e</sup> 0.2 M  $\text{HClO}_4$ . <sup>f</sup> 0.1 M  $\text{HClO}_4$ . The yield of the dimer produced in this reaction decreased with increasing perchloric acid concentration. <sup>g</sup> 1.0 M  $\text{HClO}_4$ .

The formation of  $(\text{FeOH})_2^{4+}$  in the  $\text{HOCl}$  and  $\text{O}_3$  oxidations is of particular interest, since it suggests that iron(IV) is an intermediate in these reactions. The kinetic data are consistent with the dimer being formed as shown below.



(5) G. Dulz and N. Sutin, *Inorg. Chem.*, **2**, 917 (1963).

(6) T. J. Conocchioli, G. H. Nancollas, and N. Sutin, *J. Am. Chem. Soc.*, **86**, 1453 (1964).

(7) N. Sutin, J. K. Rowley and R. W. Dodson, *J. Phys. Chem.*, **65**, 1248 (1961).

(8) R. M. Milburn and W. C. Vosburgh, *J. Am. Chem. Soc.*, **77**, 1352 (1955).

(9) R. C. Turner and K. E. Miles, *Can. J. Chem.*, **35**, 1002 (1957).

(10) We have formulated the iron(III) dimer as  $\text{Fe} \begin{smallmatrix} \text{OH} \\ \text{OH} \end{smallmatrix} \text{Fe}^{4+}$  rather than as  $\text{Fe-O-Fe}^{4+}$  since the chromium(III) dimer has been shown to possess the dihydroxy-bridged structure: R. W. Kolaczowski and R. A. Plane, *Inorg. Chem.*, **3**, 322 (1964).

(11) R. E. Connick and C. P. Coppel, *J. Am. Chem. Soc.*, **81**, 6389 (1959).

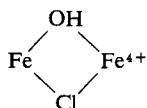
(12) R. J. Campion, T. J. Conocchioli, and N. Sutin, *ibid.*, **86**, 4591 (1964).

This scheme is similar to the one proposed<sup>13</sup> 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  $25.0^\circ$ . These rate constants were determined by mixing solutions containing  $2.1 \times 10^{-4}$  to  $4.3 \times 10^{-3} \text{ M}$  iron(III) and 0.01 to 0.1  $\text{M}$  perchloric acid with solutions containing 0.3 to 3.0  $\text{M}$  perchloric acid, each adjusted to an ionic strength of 3.0  $\text{M}$  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  $\text{Fe}^{2+}$ - $\text{HOCl}$  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  $\text{Fe}^{3+}$  (and some  $\text{FeCl}^{2+}$ ). In a similar manner, the formation of  $\text{FeCl}^{2+}$  in the  $\text{Fe}^{2+}$ - $\text{Cl}_2$  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  $\text{Fe}^{2+}$ - $\text{H}_2\text{O}_2$  reaction is of interest in view of the suggestion that this reaction involves iron(IV) as an intermediate.<sup>14</sup>

*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).

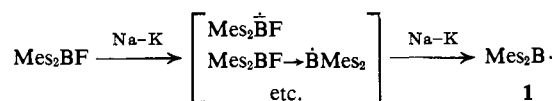
T. J. Conoccholi, E. J. Hamilton, Jr., N. Sutin  
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Received December 12, 1964

## 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

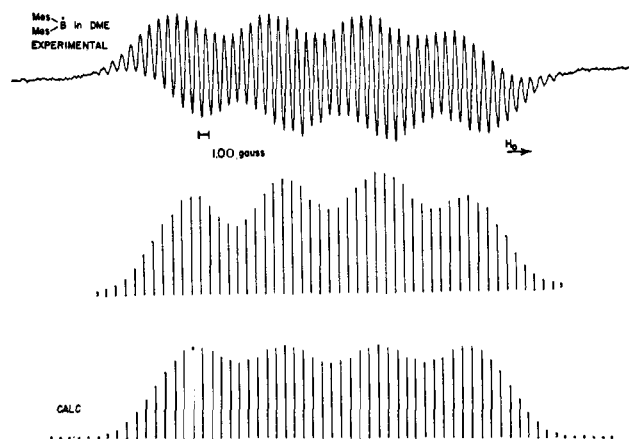


Figure 1. Observed signal and reconstructed signal of  $\text{Mes}_2\dot{\text{B}}$  assuming  $a_B = 10.0$  gauss,  $a_H = 3.0$  gauss (*meta* hydrogens), and  $a_H = 1.0$  gauss (methyl hydrogens).

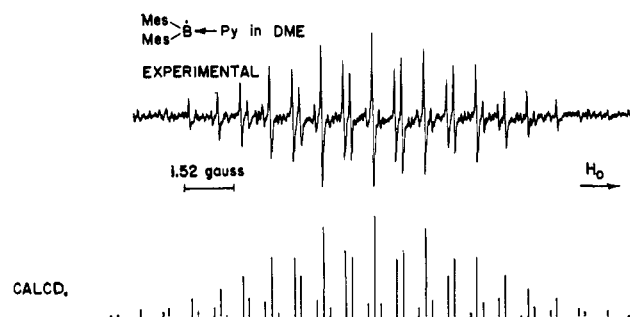
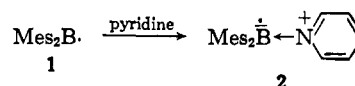


Figure 2. Observed signal and theoretical signal of  $\text{Mes}_2\dot{\text{B}}\leftarrow\text{Py}$  assuming  $a_B = a_N = 2.7$  gauss,  $a_H = 2.7$  gauss (all five pyridine hydrogens),  $a_H = 1.5$  gauss (*meta* hydrogens of the Mes groups), and  $a_H = 0$  (all methyl hydrogens).

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



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.<sup>2</sup> 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.