Iron-59 Tracer Study of the Reaction between Iron(III) Chloride and Quinolin-8-ol to give the Chlorobis(quinolin-8-olato)iron(III) Complex

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Tracer studies using ^{59}Fe show that the reaction of quinolin-8-ol and iron(III) chloride to give the chlorobis(quinolin-8-olato)iron(III) complex does not occur by a simple stepwise replacement of chloride ion.

We have previously shown[1] that the complex dichloro(quinolin-8-olato)iron(III), $FeCl_2(ox)$ (ox = quinolin-8-olato), is prepared by the reaction of iron(III) chloride (1 mol) and quinolin-8-ol (1 mol) in tetrahydrofuran and that chlorobis(quinolin-8-olato)iron(III), $FeCl(ox)_2$, is obtained when 2 mol of quinolin-8-ol is used [equations (1) and (2)]. We assumed that in the second reaction

$$2FeCl_3 + 2(oxH) \longrightarrow FeCl_2(ox) + (ox)H_2FeCl_4 \quad (1)$$

$$2FeCl_3 + 4(oxH) \longrightarrow FeCl(ox)_2 + (ox)H_2FeCl_4 + (ox)H_2Cl \quad (2)$$

$FeCl_2(ox)$ is an intermediate which reacts with additional quinolin-8-ol to give the final product. However, the $FeCl_2(ox)$ complex is insoluble and as the second reaction goes to completion (typical yields are *ca.* 90%), and is relatively fast (the reaction is complete in 15 min) we decided to test our assumption using ^{59}Fe as a tracer. It was necessary to test whether the complex $FeCl(ox)_2$ came from the reaction of quinolin-8-ol and the other product of the first reaction, tetrachloro(quinolin-8-olium)ferrate(III), because we had also shown[1] that this reaction occurs in diethyl ether–chloroform [equation (3)].

$$(ox)H_2FeCl_4 + 2(oxH) \longrightarrow FeCl(ox)_2 + (ox)H_2Cl + 2HCl \quad (3)$$

In a typical experiment $FeCl_2(ox)$ (0·75 mmol), $(ox)H_2{}^{59}FeCl_4$ (0·75 mmol), and (oxH) (1·5 mmol) were stirred in tetrahydrofuran. After 4 h separation gave a precipitate [$FeCl(ox)_2$ and $(ox)H_2Cl$] with 49·4% of the initial activity and a solution [$(ox)H_2FeCl_4$] with 50·5% of the initial activity. Equimolar quantities of $FeCl_2(ox)$ or $FeCl(ox)_2$ and $(ox)H_2{}^{59}FeCl_4$ in tetrahydrofuran showed less than 5% exchange of iron in 4—5 h.

It is clear that our previous assumption was incorrect and that the complex $FeCl(ox)_2$ does not come exclusively from the intermediate $FeCl_2(ox)$. The system iron(III) chloride–quinolin-8-ol must be complex because the results also show that the $FeCl(ox)_2$ complex does not come exclusively from $(ox)H_2FeCl_4$ either. There are a number of competitive reactions (see ref. 1 for further reactions in this system) and the precise distribution of ^{59}Fe must depend upon their relative rates. In this and, probably, related systems, it is therefore not possible to assume that a simple stoicheiometry (*e.g.* stepwise replacement of Cl by ox) occurs by a simple sequence.

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[1] M. J. Frazer, A. H. Qureshi, and F. B. Taylor, *J. Chem. Soc.* (*A*), 1971, 1712.