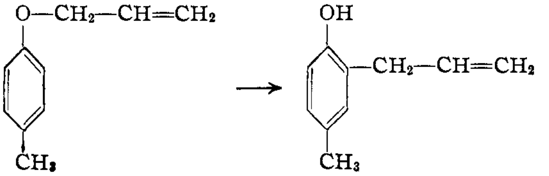
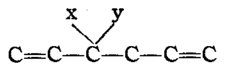
negative value for the entropy of activation of the vinyl allyl ether rearrangement is consistent with this interpretation. Three internal rotational degrees of freedom in the initial state would become vibrational degrees of freedom in the activated complex, and such a change would be accompanied by a decrease in entropy associated with the greater restriction of movement.

Assuming that the transmission coefficient was unity, Kincaid and Tarbell[5] obtained a value of -8.1 cal./deg./mole for the entropy of activation for the rearrangement of allyl *p*-tolyl ether in diphenyl ether solution



Foster, Cope and Daniels[10] studied the rearrangement of allyl groups in three carbon systems of the type



$$C{=}C{-}\overset{x\quad y}{C}{-}C{-}C{=}C$$

where the x and y are -CN or -$COOC_2H_5$ groups and obtained values of -11 to -14 cal./deg./mole for the three different compounds studied. This rearrangement is analogous to the Claisen rearrangement, also showing inversion of the allyl group, and is thought to have the same cyclic mechanism.

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Summary

1. The gas phase rearrangement of vinyl allyl ether to allyl acetaldehyde has been studied and found to be a homogeneous, first order reaction in the pressure range 15–40 cm.

2. The energy of activation is 30,600 cal. $mole^{-1}$ and the entropy of activation at 180° is -7.7 cal. $deg.^{-1}$ $mole^{-1}$. The large negative entropy of activation indicates that the reaction proceeds by a cyclic mechanism.

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(10) Foster, Cope and Daniels, THIS JOURNAL, **69**, 1893 (1947).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF LOUISVILLE]

Complexes of Ferric Iron with 8-Hydroxyquinoline-5-sulfonic Acid

BY J. P. PHILLIPS

The method of continuous variations[1] when applied to the green, soluble complex formed between ferric iron and 8-hydroxyquinoline in perchlorate solution at low *p*H values shows that the complex contains one mole of iron per mole of 8-hydroxyquinoline.[2] These results have been duplicated by this writer and others[3] for both 8-hydroxyquinoline and the related 8-hydroxyquinoline-5-sulfonic acid; with both compounds the 1:1 mole ratio of iron to reagent was observed in perchlorate solutions at various *p*H values. These facts were somewhat surprising because Molland has stated,[4] without citing sufficient experimental detail for duplication, that the complex between ferric iron and 8-hydroxyquinoline-5-sulfonic acid (referred to as HOs) has the formula $FeOs_3$, and Yoe and Hall have shown that the similar compound 7-iodo-8-hydroxyquinoline-5-sulfonic acid forms a complex containing a 1:3 mole ratio of iron to reagent.[5]

The investigation reported here was undertaken to establish whether a 1:3 complex can be formed between ferric iron and 8-hydroxyquinoline-5-sulfonic acid, and, if so, to determine under what conditions this complex exists.

Experimental

All measurements were made with a Beckman Model DU quartz spectrophotometer using 1.00-cm. cells and sensitivities such that the slit widths were less than 0.1 mm.

Standard solutions of 8-hydroxyquinoline-5-sulfonic acid were prepared by dissolving weighed samples of the reagent in water or the appropriate dilute acid. The compound was prepared by a known method,[6] recrystallized several times from dilute hydrochloric acid and dried at 110°. Calcd.: N, 6.24. Found: N, 6.09, 6.18. Standard solutions of ferric iron were prepared from ferric ammonium sulfate dissolved in dilute sulfuric acid, from pure ferrous ammonium sulfate oxidized with nitric acid, and from pure iron wire dissolved in hydrochloric acid and oxidized with hydrogen peroxide, giving, respectively, solutions of ferric sulfate, nitrate and chloride. (The small

(1) Vosburgh and Cooper, THIS JOURNAL, **63**, 437 (1941).

(2) Sandell and Spindler, *ibid.*, **71**, 3806 (1949).

(3) Merritt, Huber and Phillips, unpublished observations.

(4) Molland, THIS JOURNAL, **62**, 541 (1940).

(5) Yoe and Hall, *ibid.*, **59**, 872 (1937).

(6) Matsumura, *ibid.*, **49**, 813 (1927).

amount of sulfate present in the ferric nitrate solution did not appear to influence the results.)

Results and Discussion

Although ferric iron does not form complexes with perchlorate ion in strong acid, weakly acidic solutions of ferric perchlorate like other salts of iron contain stable complexes[7] between iron and hydroxide ion, so that a 1:1 mole ratio of iron to 8-hydroxyquinoline-5-sulfonic acid does not necessarily indicate a complex formula $FeOs^{++}$, but may result from a complex such as $Fe(OH)_2Os$. The fact that the depth of the color of the solution increases with increasing hydroxide ion concentration is a further indication that the complex may contain hydroxide.

The 1:1 ratio is always obtained in perchlorate, chloride, nitrate or sulfate solution as long as the adjustment of *p*H is made with sodium hydroxide or dilute mineral acid.[3] However, in an acetate buffer a 1:3 mole ratio of iron to 8-hydroxyquinoline-5-sulfonic acid is indicated by the several methods discussed below. That this complex differs from the one found in an unbuffered solution is shown by the absorption maxima, which occur at 445 and 580 mμ, as compared to 450 and 625 mμ for the unbuffered complex. To decide whether or not the 1:3 mole ratio in acetate solution is the chance result of an indefinite number and variety of complexes being present, a number of concentrations, anions, and methods of determining the complex formula were tried; since the 1:3 ratio is always obtained it seems probable that a single complex, perhaps $FeOs_3$, exists in acetate buffer.

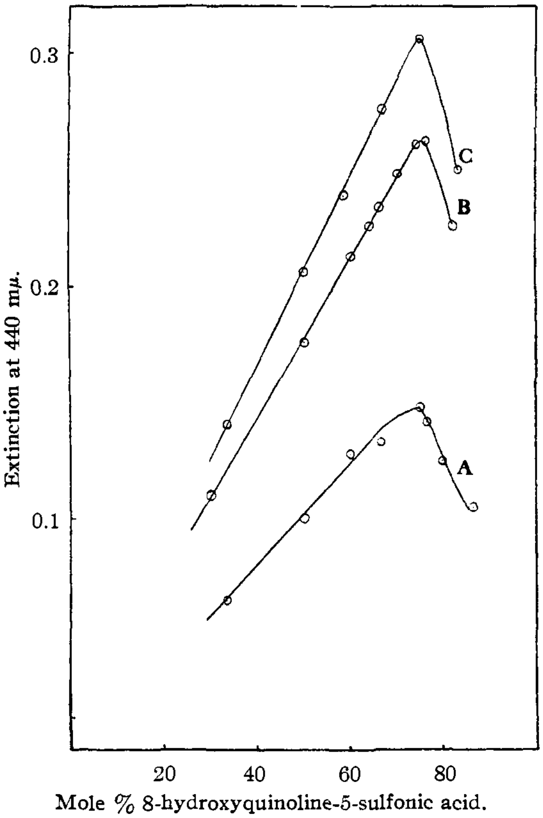

Fig. 1.—Determination of complex formula by continuous variations method in 0.1 *M* acetate buffer of *p*H 4.7. Total concentration of $FeCl_3$ plus HOs is: A, 1.2×10^{-4} *M*; B, 2.0×10^{-4} *M*; C, 2.4×10^{-4} *M*.

Method of Continuous Variations.—This well-known procedure was applied to the acetate buffered solution (*p*H 4.7) after establishing by the method of Vosburgh and Cooper that only one complex was present. Results for various concentrations of ferric chloride with the reagent (Fig. 1) at five wave lengths (440, 450, 560, 580 and 600 mμ) always showed a 75 mole per cent. 8-hydroxyquinoline-5-sulfonic acid in the complex; identical values were obtained with the corresponding concentrations of ferric sulfate and nitrate.

Owing to the relatively great uncertainty in locating the maximum in the curve precisely with this method, the other procedures described below were tried.

Mole Ratio Method.—In this procedure[8] the extinctions of solutions having varying concentrations of 8-hydroxyquinoline-5-sulfonic acid per mole of ferric iron were plotted against the ratios (Fig. 2). If the complex is stable and obeys Beer's law, a straight line is obtained until

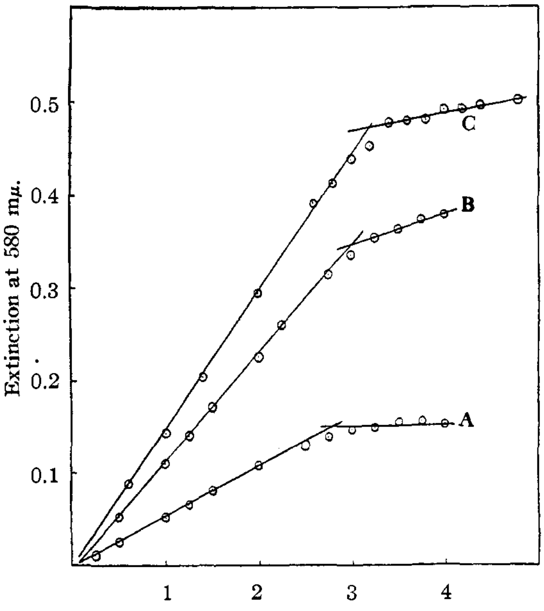

Fig. 2.—Determination of complex formula by mole ratio method in 0.1 *M* acetate buffer of *p*H 4.7: A, 4.0×10^{-5} *M* ferric nitrate; B, 8.0×10^{-5} *M* ferric iron as sulfate; C, 1.0×10^{-4} *M* ferric chloride.

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[7] Rabinowitch and Stockmayer, THIS JOURNAL, **64**, 335 (1942).

[8] Yoe and Jones, *Anal. Chem.*, **16**, 112 (1944).

the mole ratio reaches the value required for the complete formation of the complex, at which point the line breaks and becomes horizontal (or nearly horizontal if there is a slight contribution to the extinction from the large excess or reagent). Since the break always occurred at a value of 3.00 ± 0.25 moles of 8-hydroxyquinoline-5-sulfonic acid per mole of ferric iron for chloride, nitrate or sulfate solutions at various concentrations, when buffered with acetic acid and sodium acetate, a 1:3 mole ratio in the complex is again indicated.

Application of this method to phthalate buffered solutions of *p*H 4.0 also showed an approximate 1:3 value although some deviation from Beer's law occurred before the 1:3 point was reached, perhaps because of an equilibrium between the ferric phthalate complex or complexes and the $FeOs_3$ complex. In citrate solution no complex with 8-hydroxyquinoline-5-sulfonic acid was obtained.

Molland's Method.—When a complex obeys Beer's law (as shown for this complex by the mole ratio method) a method for the determination of the approximate formula using only two solutions has been developed,[4] and was applied here with some experimental simplification.

The reaction for the complex formation between iron and 8-hydroxyquinoline-5-sulfonic acid may be written

$$x\text{HOs} + \text{Fe}^{+3} \longrightarrow \text{FeOs}_x + x\text{H}^+$$

If the extinctions of two solutions, the first containing a concentration p of ferric ion and a large excess q of 8-hydroxyquinoline-5-sulfonic acid, and the second containing the same concentration p of 8-hydroxyquinoline-5-sulfonic acid and a large excess q of ferric ion, are measured, the following relation holds at wave lengths where the ferric ion and the reagent have no appreciable extinction

$$x = d_1/d_2$$

where d_1 is the extinction of the first solution and d_2 that of the second.

The ratio actually obtained for several solutions and varying concentrations at 440 mμ was 3.2 (Table I.) The fact that this value is slightly high is due to a small contribution to the total extinction of the large concentrations of 8-hydroxyquinoline-5-sulfonic acid necessary.

TABLE I

MOLLAND'S METHOD FOR ACETATE SOLUTIONS (*p*H 4.7) OF FERRIC IRON AND 8-HYDROXYQUINOLINE-5-SULFONIC ACID

Anions present	$p \times 10^5\ M$	$q \times 10^4\ M$	d_1/d_2
$SO_4^=$, OAc^-	3.20	4.00	3.23
	4.00	4.00	3.32
	4.80	6.00	3.23
	6.00	6.00	3.24
Cl^-, OAc^-	2.00	2.00	3.20
	4.00	4.00	3.00
	4.40	4.40	3.20
	4.80	4.80	3.20
		Average	3.20

On the basis of the above results it seems likely that the use of colorimetric methods for determining iron based on the reaction with 8-hydroxyquinoline, 8-hydroxyquinoline-5-sulfonic acid, and 7-iodo-8-hydroxyquinoline-5-sulfonic acid needs to be restricted to solutions of known and controlled buffer content.

Summary

1. A green complex between ferric iron and 8-hydroxyquinoline-5-sulfonic acid in acetate buffered solutions having a 1:3 mole ratio of iron to reagent and a possible formula $FeOs_3$ has been shown to be distinct from the 1:1 complex formed in unbuffered solutions.

2. Several methods for the spectrophotometric determination of complex formulas have been employed.

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