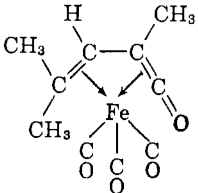
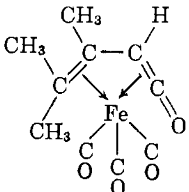
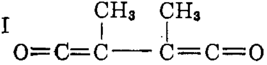
that the new iron complex is π-1,3,3-trimethylcyclopropene-iron tetracarbonyl, analogous to π-acrylonitrile-iron tetracarbonyl.[4]

The infrared and n.m.r. data given above indicate that the new iron complex consists of an iron tricarbonyl group π-bonded to a $C_6H_{10}CO$ residue which acts as a four-electron donor and which contains a single olefinic hydrogen atom and three methyl groups. The two structures which satisfy these conditions are II and III, which differ only in the relative locations of a methyl group and a hydrogen atom.


II


III


$$O{=}C{=}\overset{CH_3}{\overset{|}{C}}-\overset{CH_3}{\overset{|}{C}}{=}C{=}O$$
IV

In either of these structures an iron tricarbonyl group is π-bonded to a vinylketene derivative in a manner similar to the iron tricarbonyl complexes of various dienes.[5] Such diene complexes of vinylketene derivatives are related to diene complexes of butadiene derivatives by the replacement with an oxygen atom of the two substituents on one of the end carbon atoms of the four-carbon chain which is bonded to the iron atom.

It would be of interest to decide between structures II and III for $C_6H_{10}COFe(CO)_3$. However, the infrared and n.m.r. data do not permit an unequivocal decision between these two structures. Either a degradation of $C_6H_{10}COFe(CO)_3$ to a known compound by unambiguous methods or synthesis of $C_6H_{10}COFe(CO)_3$ from a vinylketene derivative of known structure would therefore seem to be necessary. Due to the relatively low yield of $C_6H_{10}COFe(CO)_3$, insufficient material was available for degradation studies. The instability of vinylketene derivatives and the obscurity of the vinylacetic acid derivatives which would be precursors to the desired ketenes made synthesis of $C_6H_{10}COFe(CO)_3$ from a ketene derivative of known structure unattractive. Therefore, no data were obtained which would permit an unequivocal decision between structures II and III for $C_6H_{10}COFe(CO)_3$.

Since vinylketene derivatives appear to form diene-iron tricarbonyl complexes, it seemed possible that a bis-ketene with two conjugated carbon–carbon double bonds would form similar complexes. Such bis-ketene derivatives are unknown. However, dialkylcyclobutenedione derivatives[5] might be expected to form small amounts of such bis-ketene derivatives on thermal cleavage of the four-membered ring. Nevertheless, attempts to make an iron tricarbonyl diene complex of the bis-ketene IV by the reaction between triiron dodecacarbonyl or iron pentacarbonyl and dimethylcyclobutenedione[6] were unsuccessful. Here, as in the preparation of other iron tricarbonyl complexes of unsaturated ketenes, the difficulty appears to be finding a suitable method of synthesis rather than instability of the final iron carbonyl complex since $C_6H_{10}COFe(CO)_3$ appears to be approximately as stable as other diene-iron tricarbonyl complexes.

Finally, it is of interest that both in the formation of I from 1,2,3-triphenylcyclopropenyl bromide and $NaCo(CO)_4$[2] and in the formation of $C_6H_{10}COFe(CO)_3$ from 1,3,3-trimethylcyclopropene and triiron dodecacarbonyl described above, one of the carbonyl groups of the metal carbonyl derivative is converted to a ketonic carbonyl group. The fact that products of different types are obtained in these two reactions is not surprising due to the differences in the nature of both the metal carbonyl derivatives and the cyclopropene derivative.

Acknowledgment.—The author is indebted to Mr. M. Bisnette for experimental assistance and for taking most of the infrared spectra, to Professor G. L. Closs for furnishing experimental details for the preparation of 1,3,3-trimethylcyclopropene, and to Professor A. T. Blomquist for furnishing a generous sample of dimethylcyclobutenedione.

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The Kinetics of the Formation of the Monoazide Complex of Iron(III)[1]

BY D. SEEWALD[2] AND N. SUTIN

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The red color of aqueous solutions containing ferric ions and hydrazoic acid has been known for many years. According to Ricca,[3] Wallace and Dukes,[4] and Bunn, Dainton, and Duckworth,[5] the species responsible for the red color, at least at low azide concentrations, is FeN_3^{2+}. They have presented evidence that these equilibria exist in the red solutions

$$Fe^{3+} + HN_3 \rightleftharpoons FeN_3^{2+} + H^+ \qquad K_1$$
$$Fe^{3+} + H_2O \rightleftharpoons FeOH^{2+} + H^+ \qquad K_h$$
$$HN_3 \rightleftharpoons H^+ + N_3^- \qquad K_a$$

where the coördinated water molecules are not shown. The values of K_1, K_h, and K_a are 5.91×10^{-1}, $1.65 \times$

[1] Research performed under the auspices of the U. S. Atomic Energy Commission.

[2] Summer student from Brooklyn College, Brooklyn, New York.

[3] B. Ricca, *Gazz. chim. ital.*, **75**, 71 (1945).

[4] R. M. Wallace and E. K. Dukes, *J. Phys. Chem.*, **65**, 2094 (1961).

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10^{-3}, and 7.0×10^{-5}, respectively, at 25.0° and an ionic strength of 1.00.[4-7] We have studied the rate of formation of FeN_3^{2+} at 25.0° as a function of the iron(III), azide, and perchloric acid concentrations of the solution. The rate of formation of FeN_3^{2+} is compared with the rates of formation of the mono-complexes of iron(III) with thiocyanate,[8] chloride,[9] bromide,[10] fluoride,[11] and sulfate ions.[12,13]

Experimental

Chemicals.—The iron(III) perchlorate was obtained from the G. Frederick Smith Chemical Company and was purified by recrystallization from perchloric acid. A stock solution approximately 0.5 F in $Fe(ClO_4)_3$ and 1.5 F in $HClO_4$ was prepared from the recrystallized iron(III) perchlorate. The perchloric acid (70%) was obtained from the J. T. Baker Chemical Company. The concentration of the iron(III) in the stock solution was estimated by reduction of the iron(III) with a Jones reductor and titration of the iron(II) produced with standard ceric sulfate using ferroin as indicator. A stock solution of sodium perchlorate was prepared by dissolving sodium carbonate (Baker Analyzed Reagent) in water and neutralizing to pH 5.0 with perchloric acid. The sodium perchlorate concentration was determined gravimetrically after evaporation. A 0.5 F solution of sodium azide (Fisher Scientific Company) was prepared by dissolving the appropriate weight of the compound in distilled water. The solution was standardized by the addition of excess ceric sulfate to an aliquot of the solution and back-titration of the excess ceric sulfate with ferrous sulfate.

Procedure.—The kinetics was studied by the use of a modified version of the rapid-mixing and flow apparatus which has been described previously.[14,15] The modification allowed the study of reactions with half-times ranging down to about 5 msec. by means of the stopped-flow technique. Solutions containing iron(III) at a given acid concentration and ionic strength of 1.00 were mixed with sodium azide solutions of comparable acidity and ionic strength and the rate of formation of FeN_3^{2+} was followed at 460 mμ. The other species present in the solution exhibit negligible absorptions at this wave length.

Results

The kinetic data are consistent with the assumption that the formation of FeN_3^{2+} proceeds *via* two paths, one involving the reaction of Fe^{3+} with HN_3 and the other the reaction of $FeOH^{2+}$ with HN_3, and that equilibrium between HN_3 and N_3^- and between Fe^{3+} and $FeOH^{2+}$ exists throughout the course of the reaction. Under these conditions, the rate of formation of FeN_3^{2+} is given by

$$\frac{d(FeN_3^{2+})}{dt} = k_{1f}(Fe^{3+})(HN_3) + k_{2f}(FeOH^{2+})(HN_3) - k_{1d}(FeN_3^{2+})(H^+) - k_{2d}(FeN_3^{2+}) = [k_{2f}K_h + k_{1f}(H^+)]\frac{(Fe^{3+})(HN_3)}{(H^+)} - [k_{2d} + k_{1d}(H^+)](FeN_3^{2+})$$

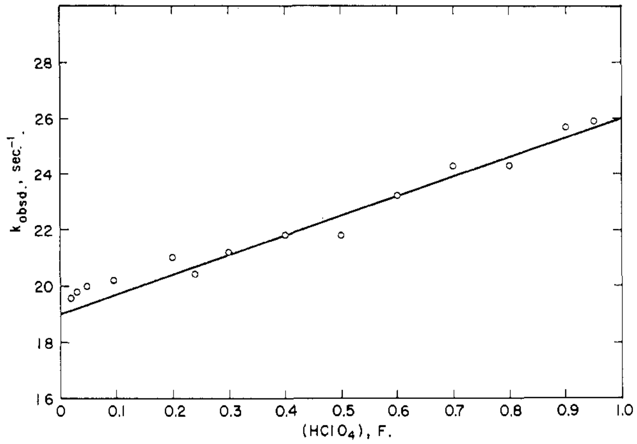

Fig. 1.—Plot of k_{obsd} *vs.* perchloric acid concentration at 25.0° and ionic strength of 1.00.

where the rate constants are defined by the equations

$$Fe^{3+} + HN_3 \underset{k_{1d}}{\overset{k_{1f}}{\rightleftharpoons}} FeN_3^{2+} + H^+$$

$$FeOH^{2+} + HN_3 \underset{k_{2d}}{\overset{k_{2f}}{\rightleftharpoons}} FeN_3^{2+}$$

At equilibrium $d(FeN_3^{2+})/dt = 0$, and since $(H^+) >> (HN_3)$ and $(Fe^{3+}) >> (FeN_3^{2+})$, it follows that

$$[k_{2d} + k_{1d}(H^+)] = \frac{[k_{2f}K_h + k_{1f}(H^+)](Fe^{3+})(HN_3)_{eq}}{(H^+)(FeN_3^{2+})_{eq}}$$

$$\therefore \frac{d(FeN_3^{2+})}{dt} = \frac{[k_{2f}K_h + k_{1f}(H^+)](Fe^{3+})_{eq}}{(H^+)} \times \left[\frac{(HN_3)(FeN_3^{2+})_{eq} - (FeN_3^{2+})(HN_3)_{eq}}{(FeN_3^{2+})_{eq}}\right]$$

Moreover, under the conditions used in this investigation $(HN_3) \approx (HN_3)_{eq}$ and therefore

$$\frac{d(FeN_3^{2+})}{dt} = \left[\frac{k_{2f}K_h}{K_1} + \frac{k_{1f}(H^+)}{K_1}\right][(FeN_3^{2+})_{eq} - (FeN_3^{2+})]$$

$$\therefore k_{obsd} = \frac{0.693}{t_{1/2}} = \frac{k_{2f}K_h}{K_1} + \frac{k_{1f}(H^+)}{K_1} \qquad (1)$$

where $t_{1/2}$ is the half-time for the formation of FeN_3^{2+}.

The value of k_{obsd} was found to be equal to 25.9 ± 1.0 sec.$^{-1}$ at 25.0°, $(HClO_4) = 0.95\ F$, and ionic strength = 1.00, and independent of the total azide and iron(III) concentrations in the region 0.984×10^{-3} to $14.76 \times 10^{-3}\ F$ and 2.56×10^{-3} to $9.59 \times 10^{-3}\ F$, respectively. It is apparent from Fig. 1 that a reasonably good linear relationship exists between k_{obsd} and (H^+), at least at the higher acidities. A linear relationship between k_{obsd} and (H^+) also has been observed by Pouli and Smith[11] in their studies of the kinetics of the formation of FeF^{2+}. The slope and intercept of Fig. 1 give values of k_{1f} and k_{2f} of 4.0 ± 1.0 and $6.8 \pm 0.5 \times 10^3\ F^{-1}$ sec.$^{-1}$ at 25.0°, respectively. The reaction between $FeOH^{2+}$ and N_3^- may contribute to the observed rate at lower acidities; however, because of the scatter of the data, the magnitude of this contribution is difficult to assess.

Discussion

The second-order rate constants for the formation of

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TABLE I

RATE CONSTANTS FOR THE FORMATION OF MONO-COMPLEXES OF IRON(III) AT 25.0°

L	$Fe^{3+} + L$ k, F^{-1} sec.$^{-1}$	$FeOH^{2+} + L$ k, F^{-1} sec.$^{-1}$	Reference
Cl^-	9.4	1.1×10^4	9
Br^{-a}	20	2.7×10^4	10
SCN^-	1.27×10^2	1.0×10^4	8
SO_4^{2-}	$(6.37 \times 10^3)^b$	3×10^5	12, 13
HSO_4^-	...	$(1.4 \times 10^5)^c$	13
F^-	$(5.0 \times 10^3)^b$	...	11
HF	11.4	$(3.1 \times 10^3)^c$	11
N_3^-	$(1.6 \times 10^5)^b$	...	This work
HN_3	4.0	$(6.8 \times 10^3)^c$	This work

[a] $T = 22 \pm 2°$. [b] Calculated on the assumption that the acid-independent path is $Fe^{3+} + X^- \rightarrow FeX^{2+}$. [c] Calculated on the assumption that the acid-independent path is $FeOH^{2+} + HX \rightarrow FeX^{2+} + H_2O$.

various mono-complexes of iron(III) are presented in Table I. The rate constants for the reactions of $Fe(H_2O)_6^{3+}$ and $(H_2O)_5FeOH^{2+}$ with chloride, bromide, and thiocyanate, respectively, are presented in the second and third columns of the table. A comparison of these columns shows that $(H_2O)_5FeOH^{2+}$ undergoes reaction more rapidly than $Fe(H_2O)_6^{3+}$. Two formulations of the reactants in the acid-independent path involving sulfate, fluoride, and azide are given; the reactants in the first formulation are Fe^{3+} and X^- and in the second $FeOH^{2+}$ and HX.

Eigen[16] and Wendt and Strehlow[12] have adopted the first formulation and consider $Fe(H_2O)_6^{3+}$ and X^- as the reactants in the acid-independent path. It is apparent from the second column of Table I that this interpretation leads, at least formally, to a marked dependence of the rate constants on the nature of the entering ligand. In order to account for this dependence Eigen and Wendt and Strehlow propose that $Fe(H_2O)_6^{3+}$ undergoes hydrolysis in the collision complex formed from the reactants, *i.e.*

$$(H_2O)_5FeH_2O^{3+} + X^- \rightleftharpoons [(H_2O)_5FeOH - HX]^{2+} \rightleftharpoons [*]^{2+} \rightleftharpoons (H_2O)_5FeX^{2+} + H_2O$$

and that the degree of hydrolysis of $Fe(H_2O)_6^{3+}$ increases with the basicity of the entering ligand. In terms of this interpretation, the relatively high rate constants for the acid-independent paths involving sulfate, fluoride, and azide reflect increasing degrees of "inner hydrolysis" of the collision complex.

On the other hand, the second formulation may be adopted and $FeOH^{2+}$ and HX considered as the reactants in the acid-independent path. In this case the rate constants for all the $Fe^{3+} + L$ reactions lie in the range of 4.0 to 127 F^{-1} sec.$^{-1}$ and the rate constants for all the $FeOH^{2+} + L$ reactions lie in the range of 3×10^3 to 3×10^5 F^{-1} sec.$^{-1}$ at 25.0°. Thus not only is the dependence of the rate constants on the nature of the entering ligand reduced in the second formulation, but the dependence of the rate constants on whether $Fe(H_2O)_6^{3+}$ or $(H_2O)_5FeOH^{2+}$ is undergoing substitution is more readily apparent. It should be noted, however, that both formulations are consistent with the kinetic data since the interconversion of the acid and base forms of the reactants is rapid enough to maintain equilibrium between them throughout the reaction; the rate constants in the two formulations are related simply by the appropriate equilibrium constants. Nevertheless, the second formulation does have the advantage of removing the apparent ligand specificity and of emphasizing that the rate constants are primarily determined by whether $Fe(H_2O)_6^{3+}$ or $(H_2O)_5FeOH^{2+}$ is undergoing reaction.

According to Connick and Stover[17] and Connick and Genser,[18] the second order rate constant for water exchange on $Fe(H_2O)_6^{3+}$ is approximately 2.8×10^2 F^{-1} sec.$^{-1}$ at 25°, where any of the coördinated water molecules may be replaced. Connick and Genser also have estimated that the rate constant for water exchange on $(H_2O)_5FeOH^{2+}$ is very roughly 100 times larger than that for water exchange on $Fe(H_2O)_6^{3+}$. The similarity of the rate constants for water exchange and complex formation and the absence of a large ligand specificity lends additional support to the view that the rates are primarily controlled by the elimination of a coördinated water molecule.[17-19]

Acknowledgment.—It is a pleasure to acknowledge stimulating discussions with Dr. R. E. Connick and Dr. J. Halpern.

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Crystalline Lithiomethyl Trimethylsilane and Some of its Properties[1]

BY JOHN W. CONNOLLY AND GRANT URRY

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We recently have isolated and characterized lithiomethyl trimethylsilane. Sommer, Murch, and Mitch[2] reported the preparation of this compound in pentane solution and studied its reaction with silicon tetrachloride to form $[(CH_3)_3SiCH_2]_4Si$. These workers, however, did not attempt to isolate the pure compound.

Satisfactory yields (about 60%) of lithiomethyl trimethylsilane can be obtained by the reaction between lithium metal and a solution of chloromethyltrimethylsilane in 2-methylpentane. Vigorous stirring during the entire course of the reaction is essential in order to minimize undesirable coupling of the product lithium

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