

ORGANIC AND BIOLOGICAL CHEMISTRY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, CASE INSTITUTE OF TECHNOLOGY]

Reaction of Ferric Chloride with Alkanes¹

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RECEIVED NOVEMBER 24, 1958

Anhydrous ferric chloride has been found to react with alkanes under comparatively mild conditions, the reactivity being in the order *tert* > *sec*, and decreasing with increase in steric factors and molecular weight. The reaction is characterized by evolution of hydrogen chloride and reduction of iron(III) to iron(II). Isooctane is unique among the alkanes investigated in that it is attacked readily by both ferric chloride and aluminum chloride. With ferric chloride the evolved gas is composed mainly of isobutane and hydrogen chloride. In contrast, aluminum chloride yielded no hydrogen chloride, the volatile product consisting predominantly of isobutane as shown by Ipatieff and Grosse. Solvent and catalytic effects in the ferric chloride-alkane reaction also were investigated.

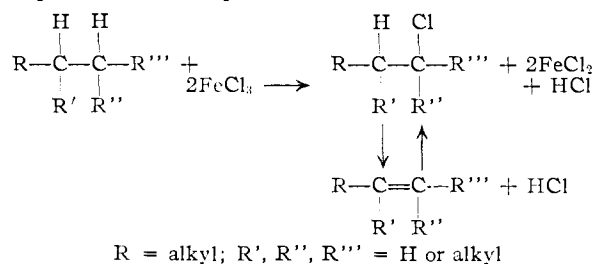
Introduction

Our objective was to study the reaction of anhydrous ferric chloride with alkanes. As far as we are aware, no previous investigators have explored this area.

A few reports are contained in the literature on the reaction of ferric chloride with alkenes. Using a vapor-phase technique, de Simo² effected chloro addition with ferric chloride to hydrocarbons containing an unsaturated linkage between two non-tertiary carbon atoms. Reaction with α -pinene yielded³ a variety of products including halogen-containing derivatives and polymers. Studies have been made⁴⁻⁶ of the interaction of ferric chloride with aromatic compounds including aralkyls. The experimental results indicate that several reactions may occur: nuclear chlorination, polymerization of aromatic nuclei, disproportionation, conversion to biaryls, polymerization involving the alkyl side chains and formation of diphenylmethane derivatives.

Results and Discussion

Alkanes. General Considerations.—The reaction of ferric chloride with alkanes occurred under comparatively mild conditions, at temperatures as low as 70° in the *tert*-series. The general reaction believed to be involved in the initial stages is expressed in the equations



(1) Paper II of the series "Reactions of Metal Halides with Organic Compounds": this paper was presented at the 133rd Meeting of the American Chemical Society in San Francisco, Calif., April 14, 1958, and is in part an abstract of a portion of the Ph.D. thesis of H. C. Volz, Case Institute of Technology, 1958.

(2) M. de Simo, Can. Patent 451,379 (1948); C. A., **43**, 3436 (1949).

(3) E. V. Zmachinskii, S. A. Maron and S. G. Shmuilovich, *J. Applied Chem. (U.S.S.R.)*, **10**, 2029 (1937).

(4) For references see P. Kovacic and N. O. Brace, *THIS JOURNAL*, **76**, 5491 (1954).

(5) R. W. Stewart, M.S. Thesis, Case Institute of Technology, 1957.

(6) P. Kovacic, R. W. Stewart and F. J. Donat, Abstracts of Papers, 131st Meeting of the American Chemical Society, Miami, Fla., April, 1957, p. 71-O.

In every case the reactive alkanes gave high yields of hydrogen chloride. Analysis of the product mixture derived from methylcyclohexane revealed the presence of iron(II) in 89% yield. The order of reactivity was based on a comparison of the temperatures (initiation temperatures) at which hydrogen chloride was first evolved after a uniform rate of heating from room temperature. From these temperatures (Table I) it is seen that *tert*-alkanes are more reactive toward ferric chloride than *sec*-alkanes, the initiation temperatures for the *sec*-alkanes being 27–68° higher than for the *tert*-compounds.

The differences in reactivity within the two series may be accounted for on the basis of a number of factors. A comparison of *n*-octane and *n*-nonane suggests that an increase in molecular weight decreases reactivity within a given homologous series.⁷ Steric influences are considered to play an important role in the *tert*-alkane group. This is indicated by the evolution of hydrogen chloride at temperatures lower for the cyclic members than for the non-cyclic ones. Furthermore, in isooctane (2,2,4-trimethylpentane) and 2,2,5-trimethylhexane the labile *tert*-hydrogen position is situated alpha or beta to a bulky *tert*-butyl group.⁸

Not as much confidence should be placed in the data for *sec*-alkanes since there is the possibility that small amounts of *tert*-alkanes, of greater reactivity than the *sec*-compounds, are present as impurities.

Certainly, initiation temperatures are a less satisfactory basis for comparison of reactivities than reaction rates at the same temperature. However, rate data may well be difficult to obtain since it is likely that products of comparable or greater reactivity, e.g., unsaturated hydrocarbons, are formed in the initial stages of reaction.

The reaction of methylcyclohexane with ferric chloride was studied in detail as an example of the ferric chloride-*tert*-alkane system and will be reported elsewhere.⁹

Isooctane.—Isooctane is unique among the alkanes studied in that it is attacked readily by both ferric chloride and aluminum chloride. A

(7) For an analogous situation involving antimony pentachloride see B. L. Moldavskii and S. E. Livshitz, *Compt. rend. acad. sci. U.R.S.S.*, **1**, 507 (1935).

(8) R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," edited by M. S. Newman, John Wiley and Sons, Inc., New York, N. Y., 1956, p. 599.

(9) P. Kovacic and H. C. Volz, forthcoming publication.

nitrogen no large difference in results was apparent (Table III). However, with both methylcyclohexane and 2,2,5-trimethylhexane in the absence of air, a slight decrease in the initiation temperature and a small increase in the rate of hydrogen chloride evolution were observed. The decision as to whether these minor effects are real must await data from more rigidly controlled experiments. In addition, the reaction with methylcyclohexane proceeded equally well in the absence of light.

Studies were made with various solvents and catalysts in order to determine the effect on initiation temperature and yield of hydrogen chloride. In most cases the additives lowered the initiation temperature, and influenced the yield of hydrogen chloride only slightly. In a semi-quantitative experiment with methylcyclohexane in nitrobenzene as solvent, the rate of gas evolution in the 70–73° temperature range was decreased although the initiation temperature was decreased (Table III). Nitrobenzene would be expected to increase the solubility of ferric chloride and at the same time alter its nature by coordination.

1HCl/1FeCl₃. In the case of the experiments reported in Tables I and III the hydrogen chloride remaining in the system at the end of the reaction was purged through the scrubber, whereas this was not done with the other experiments.

Ferric chloride appeared to be quite insoluble in the alkanes and in no case did solution occur at elevated temperatures. At the end the reaction mixtures consisted of black, or almost black, solid or tarry material in excess alkane.

Ferric Chloride and Methylcyclohexane.—A mixture of 20 ml. (0.156 mole) of methylcyclohexane and 12.7 g. (0.078 mole) of anhydrous ferric chloride was heated with stirring under nitrogen with exclusion of light. At 69.5° the presence of hydrogen chloride was first detected. A 92% yield of hydrogen chloride was obtained during 20 minutes at 69–96°. The reaction mixture was cooled, diluted with ether and extracted with three portions of water containing a small amount of hydrochloric acid. The aqueous extracts were combined, washed with ether and then heated to expel dissolved ether. Operations with the aqueous solution were performed under nitrogen. Analysis²¹ by titration with dichromate in the presence of phosphoric acid with sodium diphenylamine sulfonate as indicator revealed the presence of 0.069 mole (89%) of iron(II).

Ferric Chloride (0.078 mole) and Methylcyclohexane (0.157 mole, Eastman tech. grade) in Chlorobenzene (0.049 mole) with Solvent or Catalyst (moles, temp., % HCl)

TABLE III
CATALYTIC AND SOLVENT EFFECTS

Alkane	Mole	FeCl ₃ , mole	HCl evolved, %		Total HCl, %	Total time, min.	Temp., °C.
			Temp., °C.	In 5 min. In 10 min.			
Methylcyclohexane	0.156	0.078	70–73 ^a	38 57	92	25	70–97
Methylcyclohexane ^b	.156	.078	69–73 ^c	43 62	92	20	69–96
Methylcyclohexane ^d	.156	.078	70–73 ^e	17 26	99	30	70–96
2,2,5-Trimethylhexane	.110	.062	93–96 ^f	68 85	92 ^g	20	93–105
2,2,5-Trimethylhexane ^h	.110	.062	94–98	80 90	100	15	94–99

^a HCl was first detected at 72°. ^b Performed under nitrogen with exclusion of light. ^c HCl was first detected at 69.5°. ^d In nitrobenzene (20 ml.). ^e HCl was first detected at 53–60°. ^f HCl was first detected at 96°. ^g HCl in apparatus was not swept out at the end. ^h Performed under nitrogen.

Additional discussion of the mechanistic aspects will be deferred until the ferric chloride–alkane reaction has been explored more completely.

Acknowledgment.—We wish to acknowledge the support of this work by the National Science Foundation.

Experimental^{17–19}

Materials.—Unless otherwise indicated the alkanes were Phillips pure grade (99% minimum purity) which were extracted repeatedly with concentrated sulfuric acid (three 30-ml. portions of acid and 250 ml. of alkane) washed with water, dried, and distilled. Ferric chloride was in the form of anhydrous, sublimed powder (Matheson Co.).

Ferric Chloride and Alkanes. General Procedure.—The mixture of anhydrous ferric chloride and alkane was heated with stirring in a 100-ml., 3-necked flask. Alternatively the small-scale reactions were carried out in a 50-ml. Soxhlet flask equipped with thermometer, gas outlet tube and hand stirrer. Usually 10–30 minutes was taken to reach the initiation temperature, the temperature at which evolution of hydrogen chloride was first detected in the trap liquor. The lowest temperature listed for each experiment is the initiation temperature. The hydrogen chloride²⁰ was titrated with approximately 2 *N* sodium hydroxide solution in the presence of phenolphthalein indicator. The theoretical yield for hydrogen chloride is based upon the ratio

(17) Mr. Ralph Hodous assisted with part of the experimental work.

(18) Boiling points are uncorrected.

(19) Elemental analyses were performed by Geller Laboratories, West Englewood, N. J.

(20) Since the evolved hydrogen chloride was not swept out continuously by an applied gas stream, the figures in the tables for the amount of hydrogen chloride formed within the first 10 minutes do not include the generated gas remaining in the system.

(time: 20–40 min.): none (—, 75–104°, 76); C₆H₆NO₂ (0.049, 53–106°, 73); CH₃NO₂ (0.093, 46–82°, 71); CH₃-(CH₂)₂NO₂ (0.056, 54–101°, 72); SnCl₄ (0.086, 73–95°, 82); TiCl₄ (0.091, 68–101°, 82); SbCl₃ (0.044, 58–106°, 82); PCl₃ (0.078, 53–102°, 59); AlCl₃ (0.002, 70–100°, 82).

Ferric Chloride and Isooctane.—A mixture of 30 ml. (0.18 mole) of isooctane and 14.7 g. (0.09 mole) of anhydrous ferric chloride was heated with stirring under nitrogen. The generated gas was passed through a caustic scrubber and a portion of the water-insoluble fraction (inflammable) was collected in a sample tube by water displacement. Gas evolution began at about 75° and proceeded briskly while the temperature was kept at 70–83° for 8 minutes. Much more water-insoluble gas was evolved than could be accounted for by the nitrogen originally present in the system. The sample of water-insoluble gas collected was analyzed²² by gas chromatography and found to have the composition: isobutane, 81.4%; nitrogen, 17.3%; isobutylene, 1.4%; two unidentified components (<0.2%).

Ferric Chloride and Isooctane.—The reaction mixture from the corresponding experiment in Table II was worked up in the following manner. The organic portion of the steam distillate was separated by distillation into isooctane (0.6 mole) and 8.7 g. of product which could not be distilled at atmospheric pressure through a semi-micro Vigreux column at oil-bath temperatures.

The organic residue from steam distillation consisted of 0.4 g. of ether-insoluble solid and 8.2 g. of ether-soluble, black tar. No volatile material was obtained from the tar

(21) I. M. Kolthoff and E. B. Sandell. "Textbook of Quantitative Inorganic Analysis," 3rd edition, The Macmillan Co., New York, N. Y., 1956, p. 579.

(22) We are grateful to Dr. G. R. Brown, Jr., and Mr. T. B. Selover, Jr., of the Sohio Research Laboratories for this analysis.

on attempted distillation at 0.7 mm. with a pot temperature of 227°.

Ferric Chloride and Isooctane in Chlorobenzene.—The reaction mixture from the corresponding experiment in Table II was worked up in the following manner. The organic distillate from steam distillation was fractionated through a 15 × 1 cm. column packed with glass helices to yield isooctane (2.52 moles), chlorobenzene (1.14 moles) and *tert*-butylchlorobenzene (12.7 g.) with 4.3 g. of residue.

The organic residue from steam distillation consisted of 34 g. of black, semi-solid material.

Ferric Chloride (moles) and Alkanes (95% minimum purity) (moles, temp., % HCl) in Chlorobenzene (0.049 mole) (time: 20–25 min.): FeCl₃ (0.061), isooctane (0.121, 91–100°, 69); FeCl₃ (0.055), 2,2,5-trimethylhexane (0.109, 94–111°, 72).

Aluminum Chloride and Alkanes.—(a) A mixture of 20 ml. (0.12 mole) of isooctane (Eastman, 99.5%) and 3 g. (0.022 mole) of anhydrous aluminum chloride was heated with stirring. At about 50° water-insoluble gas began to evolve at a slow rate. At 65–70° the rate was appreciably faster and increased progressively with increase in temperature. The reaction mixture, which was heated from 40 to 98.5° during 25 minutes, yielded no hydrogen chloride.

(b) No water-insoluble gas or hydrogen chloride was evolved in the following experiments (alkane, 95% minimum purity); methylcyclohexane (0.156 mole), AlCl₃ (0.029 mole), 15 min. at 90–99°; *n*-octane (0.123 mole), AlCl₃ (0.057 mole), 40 min. at 110–118°.

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE SPRAGUE ELECTRIC CO.]

Quaternary Ammonium Polyborates¹

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RECEIVED JANUARY 13, 1959

Several quaternary ammonium polyborates have been prepared. Quaternary ammonium halides were prepared by standard methods and the halides were converted to hydroxides by reaction with silver oxide or by means of an ion exchange resin. The hydroxides were converted to polyborates by reaction with boric acid or ammonium pentaborate. The compositions of the products obtained indicate that the pentaborate is a favored form and that the fundamental unit of the pentaborate ion is H₄B₅O₁₀[−]. Some of the pentaborates have been obtained with water of crystallization, usually easily removable, while others contain one additional boric acid molecule. It is suggested that this boric acid molecule is not added to the pentaborate ion, thereby producing a true hexaborate, but rather crystallizes with certain pentaborates by virtue of a favorable size relationship between it and spaces in the crystal lattice, perhaps forming hydrogen bonds to the pentaborate ions.

The existence of polyborates is a subject which has received considerable attention. The existence of such polyborate salts as sodium tetraborate, Na₂B₄O₇, potassium pentaborate, KH₄B₅O₁₀·2H₂O, and ammonium pentaborate, NH₄H₄B₅O₁₀·2H₂O, is well established. The crystal structure of potassium pentaborate has been determined by Zachariasen.^{2,3}

Polyborate ions have been detected in solution by many workers, including Ingri, *et al.*,⁴ while Edwards⁵ has detected their presence by *pH* measurements on aqueous solutions of boric acid.

In aqueous solutions of salts, such as potassium pentaborate, fairly large concentrations of polyborate ions are obtainable, but quantitative measurements of activity (of hydrogen ion, for example) lack significance with respect to concentrations or equilibrium constants since activity coefficients of boric acid and the various ionic species are unknown. In solutions of boric acid alone, the concentrations of polyborate ions in equilibrium with monoborate ions and boric acid are quite small, hence not easily detectable, since most of the boric acid is present in the undissociated form. However, in this case, the activity coefficients are all nearly unity and activity measurements retain some value in an attempt to determine equilibrium constants and concentrations of the various species. Edwards concludes that the most important

(1) This research was performed in part under Contract No. DA-36-039-sc-71186 between the Signal Corps Engineering Laboratories, Department of the Army, and the Sprague Electric Co.

(2) W. H. Zachariasen, *Z. Krist.*, **98**, 266 (1937).

(3) A. F. Wells, "Structural Inorganic Chemistry," 2nd ed., Oxford University Press, London, 1950, p. 447.

(4) N. Ingri, G. Lagerström, M. Frydman and L. G. Sällén, *Acta Chem. Scand.*, **11**, 1034 (1957).

(5) J. O. Edwards, *This Journal*, **75**, 6151 (1953).

polyborate ions in aqueous boric acid solutions are singly charged triborate and hexaborate ions. Unfortunately, his data can be fitted as well by other combinations of polyborates, such as the combination of dimer, trimer and pentamer. If another order of magnitude in the accuracy of such measurements could be obtained, it would probably be possible to reach some definite conclusions concerning the concentrations of the various possible borate ions in aqueous boric acid solutions. In view of these difficulties associated with measurements on solutions, the nature of solid polyborate salts remains perhaps the most significant factor in an understanding of borate chemistry.

The present work comprises the preparation and identification of several quaternary ammonium polyborates. Most of these salts have the formula QH₄B₅O₁₀, where Q represents the quaternary ammonium radical, while a few correspond to this formula plus one H₃BO₃ molecule. In some cases the salt was obtained with water of crystallization, but this water could be removed by suitable heating *in vacuo*. Those salts found to have the formula QH₄B₅O₁₀ will be termed pentaborates while those with the additional boric acid molecule will be called hexaborates.

Experimental

Neutral Equivalents.—Acid neutral equivalents (A.N.E.) were determined by titration with standard HCl to brom cresol green end-point while base neutral equivalents (B.N.E.) were determined by titration with standard NaOH to phenolphthalein end-point in the presence of mannitol. The selection of indicators was based on the results of preliminary titrations performed with a *pH* meter. Values of neutral equivalents reported are the average of two or more determinations in many cases.

Calculated values of B.N.E. were obtained by assuming that each boron in the molecule would behave as a molecule