

Perchloric Acid and Some Organic Perchlorates*

BY H. BURTON AND P. F. G. PRAILL

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The history of perchlorates is summarised and various methods of preparation of the acid are noted. The action of perchloric acid and some organic perchlorates on various types of organic compounds, *e.g.*, anhydrides and ethers, is discussed with particular reference to the formation of, especially, the alkyl perchlorates and related compounds. The simple alkyl esters of perchloric acid have long been known to be highly explosive; in the free state they possess many of the properties of covalent compounds. Consequently, when experiments that can lead to their formation are carried out, the risk of serious explosion is always present.

GROWING interest in the applications of perchloric acid to analytical chemistry makes the recognition of its properties imperative. Perchloric acid and the perchlorates have a notorious reputation; this is due to numerous explosions that have been recorded (Hackl¹; Meyer and Spormann²; Kahane³; Zahn⁴; Balks and Wehrmann⁵; Young and Campbell⁶; and others to be mentioned later) and also to the lack of extensive investigations of their properties. Whilst it is not intended that the hazardous properties of perchloric acid should be belittled, it is thought that a better understanding of its character may dispel some of the fears that have

* Much of the chemistry of perchloric acid and perchlorates is summarised in "The Chemical Elements and Their Compounds," by N. V. Sidgwick, Oxford University Press, 1950, pp. 1230 to 1236; see also—

Gmelin's "Handbuch der Anorganischen Chemie," Eighth Edition, System No. 6, "Chlor," Verlag Chemie, Berlin, 1927, pp. 362 to 409.

"Perchloric Acid," Volume I, Second Edition, G. Frederick Smith Chemical Co., Columbus, Ohio, 1933.

"Mixed Perchloric, Sulphuric and Phosphoric Acids and Their Applications in Analysis," G. Frederick Smith Chemical Co., Columbus, Ohio, 1935.

E. Kahane, "L'Action de l'Acide Perchlorique sur les Matières Organique et ses Applications a la Chemie Analytique," Hermann et Cie, Paris, 1934.

A. Vialard-Goudu, "Contribution à l'Étude de l'Acide Perchlorique, Action sur les Composés Organiques," Danel, Lille, 1937.

prevented its general use. We wish to emphasise the distinction between anhydrous perchloric acid and the 70 to 72 per cent. solution of the acid that is obtainable commercially. In this account, perchloric acid will refer to the solution, unless otherwise stated.

The history of the perchlorates begins with the discovery of potassium perchlorate by Stadion⁷ in 1816. Stadion observed the formation of the salt in cooled mixtures of potassium chlorate and concentrated sulphuric acid. He prepared an aqueous solution of perchloric acid from the new salt. A simple ester, ethyl perchlorate, was prepared by Hare and Boye⁸ as early as 1841, by the distillation of a concentrated solution of barium ethyl sulphate and barium perchlorate. The hazardous nature of the preparation and the instability of the product were soon recognised. Subsequent observations that anhydrous perchloric acid reacted explosively with organic materials, such as alcohol, ether, wood or paper (Roscoe⁹), seem to have acted as a deterrent to further investigations. It is as well to remember that, often, concentrated aqueous solutions of the acid can behave in the same way if they become absorbed in suitably porous media, *e.g.*, wood, linoleum or grain; such mixtures are very sensitive to impact and heat (Elliott and Brown¹⁰; Kabic¹¹).

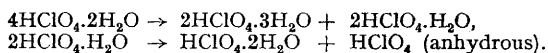
Various methods of preparing the acid have been recorded. Most of these are based on the reaction of sulphuric acid (Roscoe⁹; Vorlander and Von Schilling¹²; van Emster¹³; Mathers¹⁴) or hydrogen chloride (Kreider¹⁵; Smith and Friedman¹⁶) with metal perchlorates, or on the thermal decomposition (Serullas¹⁷; Hampel¹⁸) or electrolysis (Goodwin and Walker¹⁹; Schumacher²⁰) of chloric acid—



Hydrofluosilicic acid has been used in place of sulphuric acid (Roscoe⁹; Caspari²¹). Nitrogen-free perchloric acid can also be prepared from mixtures of ammonium perchlorate and nitric acid (Willard²²).

Aqueous solutions of the acid can be concentrated at atmospheric pressure to an azeotropic solution containing 72.4 per cent. of perchloric acid, which boils at 203° C. Distillation of this solution at ordinary pressure is accompanied by some decomposition to chlorine, chlorine oxides and oxygen. At pressures of 2 to 7 mm of mercury, the solution can be concentrated to 73.6 per cent. of acid; this corresponds to the dihydrate (Smith and Goehler²³). Aqueous perchloric acid is a colourless, hygroscopic, oily liquid ($d_{25} \approx 1.7$), which is much less dangerous than the anhydrous acid.

The latter can be prepared as a colourless mobile liquid ($d_{20} \approx 1.767$) from the aqueous solution by distillation under very carefully controlled conditions (Goehler and Smith²⁴). The following series of interesting reactions result in the formation of about 10 per cent. yields of the anhydrous acid—



A more recent method for producing the acid in high yields (greater than 70 per cent.) involves reaction of the hydrated acid with fuming sulphuric acid (Smith²⁵).

Anhydrous perchloric acid boils undecomposed at 16° C at 18 mm (van Wyk²⁶), but cannot be distilled without decomposition at ordinary pressure. Its extrapolated b.p. at 760 mm is 130° C and its m.p. is -112° C (Smith²⁵; van Wyk²⁶). On keeping, the anhydrous acid gradually becomes coloured owing to the formation of decomposition products. When this occurs, it may explode spontaneously. Pure samples do not explode when stored for about 30 days at ordinary temperatures, and they may be stored for as long as 60 days at liquid-air temperatures without the formation of colour (Smith²⁵). Perchloric acid dissolves in water with the evolution of much heat (Berthelot²⁷; Goodeve and Marsh²⁸). It is this large heat of solution that undoubtedly initiates the explosive reaction of the anhydrous acid with organic solvents. The acid forms a number of hydrates (van Wyk²⁶), the most interesting of which is the monohydrate. The X-ray diagram of this compound is analogous to that of ammonium perchlorate (Volmer²⁹), and the Raman spectrum has the characteristic absorption of the ClO_4^- ion (Fonteyne³⁰; Redlich, Holt and Bigeleisen³¹; Millon³²). Hence, the monohydrate is to be considered as the salt, hydroxonium perchlorate, $\text{H}_3\text{O}^+\text{ClO}_4^-$ (Smith and Goehler³³).

In its chemical properties, perchloric acid differs considerably from periodic acid and from chloric acid, in that it is a poor oxidising agent at ordinary temperatures. At elevated temperatures, however, its oxidising properties are considerable. As might be expected

from the preceding discussion, both the anhydrous acid and concentrated aqueous solutions of the acid are strong dehydrating agents.

Perchloric acid was formerly regarded as the strongest acid known; recently, however, it has been shown (Gillespie³⁴) that in concentrated sulphuric acid it is weak compared with substances such as disulphuric acid ($H_2S_2O_7$). It cannot be over-emphasised that the strength of an acid is dependent on the basicity of the solvent in which it is dissolved. Perchloric acid is a relatively strong acid in many organic solvents, but it must not be assumed that the strength of the acid in such solutions is necessarily comparable to its strength in water. The anhydrous acid is strongly ionised in nitromethane (Wright, Murray-Rust and Hartley³⁵) and considerably so in nitrobenzene (Murray-Rust, Hadow and Hartley³⁶).

When anhydrous perchloric acid is mixed with an organic solvent, its molecules become modified, and it is these modifications that must form the basis of our subsequent discussion. Solvation of the perchloric acid molecule will almost certainly induce a change in the polarity of the bond uniting the hydrogen atom and the perchlorate group, that is, it may become more polar than in the original molecule. The formation of a conjugate acid, as in the formation of acetic acidium perchlorate, $[AcOH_2]^+ClO_4^-$, from acetic acid, can be considered to represent the extremity of this process. These conjugate acid perchlorates may exist almost entirely as ion pairs or they may dissociate into free, or solvated, ions. The extent of this dissociation will govern the strength of perchloric acid in the solvent and hence its usefulness as a strong acid for analytical procedures in anhydrous media. If the conjugate acid is unstable, it may react other than as a solvated proton, *e.g.*, the ion $[Ac_2OH]^+$ may act as an acylating agent.

Subsequently the perchloric acid may undergo a more pronounced change, as in the formation of an ester from an alcohol. Alternatively, the perchloric acid may form an organic perchlorate without the intervention of a conjugate acid, *e.g.*, when it adds across a double bond in an unsaturated molecule.

Usually, under conditions in the neighbourhood of room temperature, the properties of these solutions are largely dependent on the weak nucleophilic properties of the perchlorate ion. As the conditions become more drastic, the oxidative character of the ion becomes more pronounced, and here another application of perchloric acid is exemplified. The point at which these two properties begin to overlap differs with the system involved and must be determined each time by careful consideration of the system and by experiment.

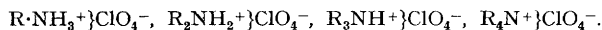
In the discussion that follows it will be seen that the usefulness of perchloric acid stems from three properties: (a) its ability to form sparingly soluble salts with many organic bases, (b) its properties as a strong acid in non-aqueous solution and (c) its oxidative properties at relatively high temperatures.

ORGANIC SALTS OF PERCHLORIC ACID

The substances to be considered in this section are those in which the central atom has a complete outer electron shell of eight electrons, as in the oxonium, sulphonium and ammonium salts. Carbonium perchlorates, in which the central atom has an outer shell of six electrons, are more profitably discussed in the later sections.

The fact that perchloric acid forms well-defined crystalline salts with basic materials, such as alkaloids, has been known for a long time (Fraude³⁷). In 1910 it was suggested that concentrated perchloric acid might be used with advantage for the isolation and identification of many ketones and feebly basic nitrogen derivatives, especially those that do not form picrates (Hofmann *et al.*^{38,39}). An additional advantage is that perchloric acid is more readily eliminated from its salts than picric acid is from picrates.

It has been pointed out by Hofmann *et al.*⁴⁰ that the solubility of the ammonium salt usually decreases in the order—



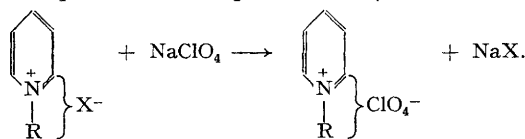
Compounds with more than one active centre, *e.g.*, benzidine, may form mono- and di-perchlorates. Many of these salts decompose explosively on heating, *e.g.*, aniline perchlorate explodes at 250° C (Spallino⁴¹). The temperature of ignition (not the *explosion temperature*) of many perchlorates of this type is in the region of 250° to 300° C (Datta and Chatterjee⁴²).

A method for the purification of pyridine via the perchlorate (Arndt and Nachtway⁴³) has sometimes led to explosions (Zacherl⁴⁴; Kahn and Oltin⁴⁵). It would seem that the explosion could be caused by traces of ethyl perchlorate, or more likely ammonium perchlorate,

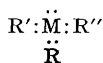
which lower the kindling temperature of the mixture. However, Moureu and Munsch⁴⁶ consider that the explosions were probably due to traces of chlorates. A method that precludes danger by avoiding the use of alcohol and ammonia has recently been developed (Arndt and Severge⁴⁷). Pyridine perchlorate exists in the form of colourless needles, m.p. 288° C, decomp. at 335° to 340° C. It can be detonated by a blow from a hammer.

Diazonium perchlorates generally have low solubilities in water. The dry salts explode violently and some, *e.g.*, *o*-tolylidiazonium perchlorate, even in the damp state (Hofmann and Arnoldi⁴⁸).

Quaternary ammonium perchlorates can be prepared by double decomposition reactions, *e.g.*, pyridinium perchlorates can be made by pouring the quaternary alkyl sulphate or toluene-*p*-sulphonate into aqueous sodium perchlorate (Allen and Wilson⁴⁹)—



Oxonium and sulphonium salts are characterised by the structure—



in which the groups R, R' and R'' may be alkyl, aryl or hydrogen. In general, the sulphonium salts are more stable than the corresponding oxonium derivatives.

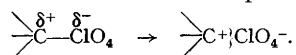
Compounds of the type $\text{R}_2\text{OH}^+\text{ClO}_4^-$ (I) are readily hydrolysed; those of the type $\text{R}_3\text{O}^+\text{ClO}_4^-$ (II), where R_3 represents a cyclic structure, are not (Hofmann *et al.*⁴⁰). Salts of the type $\text{R}_3\text{O}^+\text{X}^-$ (III), where R_3 represents three alkyl groups, are very unstable (Meerwein *et al.*⁵⁰). Examples of compounds of type I are found in the loose-addition compounds of perchloric acid with ketones or with ethers, *e.g.*, dioxan (Smeets⁵¹). Aromatic ketones form highly coloured perchlorates (Pfeiffer *et al.*⁵²), which have characteristic decomposition points. These compounds often decompose spontaneously on keeping, to give perchloric acid and the ketone, *e.g.*, *p*-methoxybenzophenone perchlorate consists of yellowish-brown unstable crystals, whilst benzalacetophenone perchlorate can be isolated as fine yellow needles, which remain stable for 5 to 6 days.

Substances of type II are familiar in the form of compounds that contain a pyran nucleus, *e.g.*, the benzopyrylium, flavylium, xanthylium and the corresponding pyronium salts. Whether many of these compounds should be considered as oxonium salts or as carbonium salts has been the object of much discussion (Hill⁵³; Shriner and Moffett⁵⁴), but need not be considered here.

This section has been based on one of the most important classical applications of perchloric acid, and many hundreds of perchlorate salts of the above types have been prepared. No attempt has been made to catalogue these; rather it has been the purpose to give a general idea of the principles involved in their formation. Most of these compounds have characteristic crystalline properties and decomposition points. Little hazard is involved in handling them (except the diazonium salts), unless they are overheated or detonated.

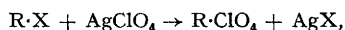
PERCHLORIC ESTERS AND RELATED COMPOUNDS

In addition to forming salts such as the above, perchloric acid is able to interact with suitably constituted organic materials to form alkyl, aralkyl, acyl or aroyl perchlorates. These substances are distinguished by having a perchlorate group directly attached to carbon. As yet, there is no evidence for perchlorates in which the perchlorate group is directly attached to an aromatic ring. We shall see that many of these compounds are mainly covalent in their properties and that others behave as typical salts. This obviously depends on the degree of polarisation of the bond between carbon and the perchlorate group—

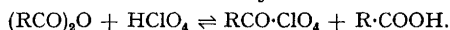


Relatively few of these substances have been isolated, and in many instances their physical properties have not been determined owing to their instability. However, it is

possible to produce many of the perchlorates in solution by metathetical reactions of alkyl, or acyl, halides with silver perchlorate—



or by the action of perchloric acid on acid anhydrides—

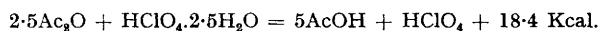


These solutions resemble those containing the corresponding compounds from other strong acids, *e.g.*, the hydrogen sulphates or sulphates, the chloroaluminates, the trifluoroacetates, and so on. For example, the perchlorates can act as alkylating or acylating agents in modified Friedel-Crafts reactions. Some consideration will be given to reactions of this type, partly because they have been of special interest to us and partly because they may play a significant role in the initial stages of certain analytical processes, such as titrations or destructions.

THE SYSTEM: ACETIC ACID - ACETIC ANHYDRIDE - PERCHLORIC ACID

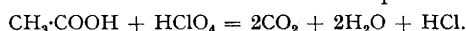
One of the most extensively investigated organic perchlorates is acetyl, or acetylium, perchlorate, $CH_3CO \cdot ClO_4$. This is mainly because mixtures of acetic anhydride and perchloric acid have been widely used for acetylation and for polishing metal surfaces in metal finishing processes.

When aqueous perchloric acid is added to acetic anhydride, rapid combination of water with the anhydride occurs, with the evolution of a considerable amount of heat (Kahane⁵⁵), *e.g.*—



The resulting solution may be considered as a solution of anhydrous perchloric acid in acetic acid, together with acetic anhydride if this was used in excess. Some disastrous explosions have been caused by these mixtures (Kuney⁵⁶), so their explosive properties have been examined rather more than have those of other organic perchlorates (Medard, Jacquet and Satorius⁵⁷; Jacquet⁵⁸; Medard and Satorius⁵⁹).

The most explosive mixture is the one in which complete combustion occurs—



The above authors state that in comparison with practical explosives the effect is mediocre. However, such mediocrity is of little consolation when the effects of explosion under laboratory conditions could lead to serious injury, or worse!

A rough calculation will illustrate the potentialities of an explosion from a mixture such as the above. Assuming the equation represents an approximation to the truth, molar quantities of acetic and perchloric acids under explosion conditions give rise, almost instantaneously, to five molecules of gas, *i.e.*, $5 \times 22 \cdot 4$ litres at S.T.P. A second and very rough approximation, that the ideal gas laws hold under these conditions, gives the volume of gases at the explosion temperature, which is about $2500^\circ C$, as 1137 litres. That is, 1 g of mixture gives about 7 litres of gas.

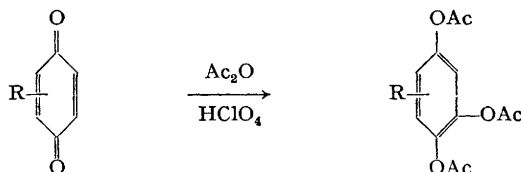
Mixtures containing less than 55 per cent. by volume of perchloric acid are incapable of detonation, and it has been shown that mixtures prepared by using perchloric acid with a density of less than 1.5 are not explosive. Further, the mixtures are less apt to explode if the ratio of acetic anhydride to acid is high. Finally, it should be mentioned that all the explosions that have been investigated have been due to the use of potentially dangerous mixtures together with faulty equipment or technique.

It is possible that in the solutions under discussion the following entities could occur: acetic acidium perchlorate, $AcOH_2^+ \{ClO_4^-\}$; acetic anhydridium perchlorate, $Ac_2OH^+ \{ClO_4^-\}$; acetylium perchlorate, $Ac^+ \{ClO_4^-\}$ (Burton and Prail⁶⁰): the formation of $Ac_3O^+ \{ClO_4^-\}$ (Usanovitsch and Jatzimirski⁶¹) has also been postulated.

The acid-catalysed acetylation of alcoholic and phenolic hydroxyl groups is well known. For example, acetylation of glucose (Kruger and Roman⁶²) and cellulose⁶³ is rapidly and efficiently performed in the cold, with acetic anhydride plus a trace of perchloric acid. The method has been extended to the acetylation of other sugars and polyhydric alcohols (Nicholas and Smith⁶⁴). It has been found, however, that anomerisation of sugar acetates occurs very readily in the presence of perchloric acid (Painter⁶⁵). For example, β -glucose pentacetate is rapidly converted to an equilibrium mixture containing about 90 per cent. of the α -anomer. Certain acid-sensitive alcohols of the type $R \cdot CH(OH) \cdot CH_2 \cdot NO_2$, where R is an aromatic nucleus, may be acetylated by similar treatment (Burton, Duffield and Prail⁶⁶). The

method is also useful for acetylating steroid compounds (Whitman and Schwenk⁶⁷; Barton *et al.*⁶⁸) and certain alkaloids, *e.g.*, cevadin (Stoll and Seebeck⁶⁹).

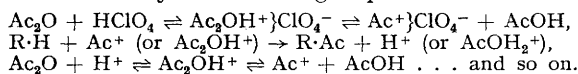
This reagent has been found to be one of the most efficient for carrying out the Thiele acetylation of quinones (Mackenzie and Winter⁷⁰; Burton and Prail^{71,72}), *i.e.*—



The corresponding triacetates are produced in good yields, even from relatively unreactive materials such as 2-methyl-1:4-naphthaquinone.

The formation of a C-C bond by solutions of acetyl perchlorate, especially in nitromethane, has been shown to occur in the acylation of suitably constituted aromatic compounds such as anisole (Burton and Prail^{60,73}), *m*-xylene and, to a less extent, toluene (Burton and Prail⁷⁴). Ketones such as acetophenone or *p*-methylacetophenone also react; these give benzoylacetone and *p*-toluoylacetone, respectively. These compounds are possible intermediates in the formation of certain pyrylium salts prepared by the action of hot acetic anhydride and perchloric acid on acetophenone or toluene (Diels and Alder⁷⁵). In this connection it is interesting to recall the self-acetylation of acetic anhydride (Burton and Prail⁶⁰).

All these reactions are readily explained by considering acetyl perchlorate to give rise to the electrophilic acetyl carbonium ion, acetylium, CH_3CO^+ . In the presence of acetic anhydride, the formation of acetic anhydridium ions, Ac_2OH^+ , and acetylium ions leads to acetylation. Experiments with acetyl chloride and silver perchlorate mixtures (Burton and Prail⁷³) indicate that the acetic anhydridium ions are less effective than the acetylium ions. The catalytic action of perchloric acid in these experiments is important because it means that often only relatively small amounts of perchloric acid need be used. The hazards from explosive oxidation are consequently reduced. This catalytic action in the presence of acetic anhydride is illustrated by the following sequence of reactions—



The possibility of the formation of these ions is strengthened by other evidence, such as the acidity of acetyl perchlorate (Mackenzie and Winter⁷⁰), and some kinetic evidence (Painter⁶⁵; Mackenzie and Winter⁷⁰). The low conductivity of acetyl perchlorate in liquid sulphur dioxide (Seel and Bauer⁷⁶) would indicate a small dissociation into ions in this solvent.

At room temperature the acetic acidium ion, $\text{CH}_3\text{COOH}_2^+$, has no acetylating properties, even towards such reactive compounds as quinol (Burton and Prail⁶⁰). Experiments by Hall, Conant and Werner^{77,78,79,80} on the system acetic acid - perchloric acid have led to a useful method for estimating weak bases. This method is dependent on the fact that weak bases appear stronger when water is replaced by a more acidic solvent. Titration can be conducted potentiometrically or by use of an indicator, *e.g.*, crystal violet. The perchloric acid in glacial acetic acid can be prepared as described above, that is, by adding the 72 per cent. aqueous solution to the calculated amount of acetic anhydride. It is advisable to keep the mixture below 20° C to prevent discolouration of the solution.

Potassium hydrogen phthalate has been recommended as a primary standard (Seaman and Allen⁸¹; Markunas and Riddick⁸²). The standardised solution can then be used for titrating such substances as amino-acids or various salts of carboxylic acids. Many inorganic salts can be titrated by this means, especially if mercuric acetate is added to the substance being titrated (Pifer and Wollish⁸³). Crystal violet undergoes a number of colour changes, *i.e.*, violet \rightarrow blue \rightarrow green \rightarrow yellow, and the colour change at the end-point depends on the system involved. It is therefore advisable to determine the colour at the potentiometric end-point. Many other indicators and solvents, including mixed solvents, have been used for a wide variety of estimations of this acid - base type, and the subject has recently been reviewed (Irving⁸⁴; Stagg⁸⁵; Riddick⁸⁶). High-frequency oscillometer techniques (Wagner and Kauffman⁸⁷) and spectrophotometry (Reilly and Schweizer⁸⁸) have increased the range

of these titrations in non-aqueous media. Perchloric acid is much better for this type of determination than sulphuric acid, which undergoes secondary reactions more readily with the other reagents, or than hydrogen chloride, which suffers disadvantages from its volatility.

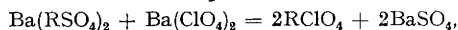
The intense colours that perchloric acid gives with various substances can often be made the basis of methods for their determination. For example, the intense red colour given by tryptophan in the presence of carbohydrate and perchloric acid has been used for determining deoxyribosenucleic acid (Cohen⁸⁹) and for measuring tissue destruction in cases of burning (Keyser⁹⁰). Recently, a new colour reaction for steroids, which utilises perchloric acid, has been reported (Tauber⁹¹).

It is very unlikely that there is any danger in the use of these techniques provided that local overheating effects are avoided.

ALKYL AND ARALKYL PERCHLORATES—

Reference has already been made to the early preparation of ethyl perchlorate by Hare and Boye⁸ (p. 5). Esters of the type $\text{HO}(\text{CH}_2)_2\cdot\text{O}\cdot(\text{CH}_2)_2\cdot\text{ClO}_4$ and $\text{Cl}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{ClO}_4$ were prepared by Hofmann and his collaborators⁹² by the action of 60 per cent. perchloric acid on ethylene oxide and epichlorohydrin, respectively. These compounds are colourless oils that explode on heating or on percussion.

In 1936, Meyer and Spormann⁹³ re-investigated the preparation and properties of some alkyl perchlorates. Methyl, ethyl and propyl perchlorates can all be prepared by distillation of the barium alkyl sulphate with barium perchlorate—



or by the reaction of the alkyl halides with a solution of silver perchlorate in ether; cautious evaporation of the ethereal solution then gives the ester.

Methyl perchlorate can also be prepared by the reaction between anhydrous perchloric acid and diazomethane in dry ether (Meyer and Spormann⁹³)—



The esters are colourless oils; the methyl ester boils at about 52° C, the ethyl ester at 89° C. They are very powerful explosives and are considerably more sensitive than the corresponding nitrate esters. Meyer and Spormann took considerable precautions when studying these compounds. They stated that, in spite of the greatest foresight, it was not possible to avoid explosions of the ester (one author, W. S., lost the tips of three fingers). We hold it impossible to over-emphasise that the simple alkyl esters are extremely dangerous in the free state. In this connection, mention should be made of a number of accidents (Hillebrand and Lundell⁹⁴; Knuth⁹⁵; Deiss and Meyer⁹⁶) resulting from the standard method for determining perchlorates or potassium, *i.e.*, as the sparingly soluble potassium perchlorate. Explosions have occurred when attempts have been made to concentrate the aqueous-alcoholic filtrate after the separation of most of the potassium salt. This may be due to traces of residual perchloric acid or to the formation of the highly explosive ethyl ester. Attempts to recover alcohol from such solutions should be strongly discouraged.

The alkyl perchlorates are not miscible with water and are only slowly hydrolysed by it. This behaviour parallels that shown by chlorine heptoxide, Cl_2O_7 , which reacts only slowly with water (Michael and Conn⁹⁷). This is explained (Goodeve and Marsh²⁸) by the fact that perchloric acid has a limited solubility in the heptoxide and forms a protective sheath round the drop. The water diffuses slowly through this protective sheath and so hydrolysis proceeds only slowly. If a solution of ethyl perchlorate in alcohol is added to alcoholic potassium hydroxide, the immediate precipitation of potassium perchlorate occurs.

Little is known about the chemical properties of these compounds. We have found⁹⁸ that methyl perchlorate, formed *in situ* from methyl iodide and silver perchlorate, alkylates anisole in the *para* position. The metathetical reaction between the primary alkyl halides and silver perchlorate is relatively slow (Burton and Prail⁹⁸; Redies and Iredale⁹⁹). As would be expected, the reaction with tertiary halides, *e.g.*, *tert.*-butyl chloride, is much more rapid. If the reaction is carried out in benzene, *tert.*-butylbenzene and *p*-di-*tert.*-butylbenzene can soon be isolated (Burton and Prail¹⁰⁰). Further evidence for the alkylating properties of *tert.*-butyl perchlorate is given by the formation of 4-*tert.*-butylphenol and 2:4-di-*tert.*-butylphenol in mixtures of phenol, *tert.*-butanol and perchloric acid (Sears¹⁰¹). The alkylation of toluene by *cyclohexyl* perchlorate has also been reported (Cauquil and Barrera¹⁰²; Cauquil, Barrera and Barrera¹⁰³).

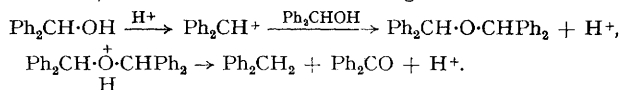
The interesting trichloromethyl perchlorate, $\text{CCl}_3\text{-ClO}_4$, is formed by metathesis of carbon tetrachloride with silver perchlorate in the presence of traces of hydrogen chloride (Birckenbach and Goubeau¹⁰⁴). It is a colourless explosive mobile liquid, which begins to decompose at 40°C . The ester is miscible with carbon tetrachloride; it reacts with ethylene dibromide and phosphorus oxychloride.

THE ARALKYL PERCHLORATES—

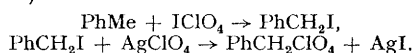
The arylmethyl perchlorates form a closely related series of compounds, which show a progressive increase in stability as each hydrogen of the methyl group is replaced by phenyl.

Triarylmethyl perchlorates are typical carbonium salts, as illustrated by their relatively high conductivity in non-aqueous media (Hofmann, Kirmreuther and Thal¹⁰⁵; Lifschitz and Girbes¹⁰⁶; Ziegler and Wollschitt¹⁰⁷) and by their absorption spectra (Hantzsch¹⁰⁸; Anderson¹⁰⁹). These perchlorates were among the first carbonium salts to be prepared (Gomberg¹¹⁰; Gomberg and Cone¹¹¹). They are readily formed by the action of perchloric acid on the corresponding carbinols, or by metathesis of the chloride with silver perchlorate in a suitable solvent, *e.g.*, nitrobenzene. The triarylmethyl perchlorates are beautifully crystalline materials of relatively high melting point and are usually highly coloured. In fact, Brand, Gabel and Rosenkranz¹¹² made use of the disappearance of the colour of the perchlorate by titration with alcohol in order to determine the relative stability of the salts.

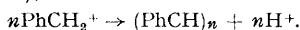
Although much of the information about the triarylmethyl perchlorates must be applicable to the diarylmethyl salts, the latter have not been investigated very extensively. However, diphenylmethyl perchlorate, prepared *in situ* from diphenylmethyl chloride and silver perchlorate, converts benzene to triphenylmethane in good yield at room temperature (Burton and Cheeseman¹¹³). With diphenylmethanol and perchloric acid in benzene, the main products are bisdiphenylmethyl ether, benzophenone and diphenylmethane; smaller amounts of triphenylmethane are also produced. These results have been interpreted (Burton and Cheeseman¹¹⁴) in terms of the following reactions—



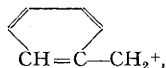
The properties of benzyl perchlorate show that it is an exceedingly reactive substance. So much so, in fact, that it rapidly polymerises in solution unless it reacts with the solvent (Burton and Prail¹¹⁵). The substance was probably first prepared by the reaction, in sunlight, of iodine and silver perchlorate with toluene, but only polymeric materials were isolated (Birckenbach and Goubeau¹¹⁶)—



It has been shown that benzyl perchlorate reacts rapidly with benzene or toluene to give high yields of diphenylmethane and *p*-methyl-diphenylmethane, respectively (Burton and Prail^{98,115}). The ready formation of these products has been ascribed to the high reactivity of the benzyl cation, PhCH_2^+ . In a solvent in which no such alkylation occurs, *e.g.*, nitromethane, there is evidence of polymerisation of the benzyl cation (Burton and Prail¹¹⁶; Monicelli and Hennion¹¹⁷), thus—



The benzyl cation may be regarded as a special case of the substituted allyl cation—



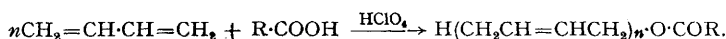
and it is interesting to note that other substituted allyl cations polymerise readily under similar conditions (Burton and Munday¹¹⁸).

Evidence for the intermediate formation of the benzyl cation in the debenylation of certain aromatic ethers by acetylium perchlorate has been obtained (Burton and Prail¹¹⁹), and there is some indication that relatively unreactive ethers, *e.g.*, methyl ethers, may be split by this reagent. The possible formation of alkyl perchlorates by reactions of this type must always be borne in mind.

Some evidence for the possible explosive character of benzyl perchlorate is given by

the explosion that occurred when an attempt was made to destroy benzylcelluloses by boiling with perchloric acid (Sutcliffe¹²⁰).

Most of the above data refer to reactions in which an alkyl perchlorate is definitely formed; this may undergo subsequent fission to carbonium and perchlorate ions. A second type of reaction to be considered is one in which a proton from perchloric acid reacts with a molecule to give a carbonium ion, which may, momentarily at any rate, exist as the alkyl perchlorate. As an example of this kind of reaction we may consider the telomerisation of butadiene and of isoprene (Jenner and Schreiber¹²¹; Jenner¹²²) to give a number of esters, *e.g.*—



Sufficient has now been said to illustrate the potentialities of perchloric acid in reactions of this type. Clearly, it is not merely the presence of anhydrous perchloric acid in organic solution that causes the explosive reactions observed by Roscoe.⁹ However, the mixtures that have been mentioned may contain up to 10 per cent. w/v of the anhydrous acid and must therefore be considered as potentially explosive. Among the main characteristics of an explosive are its sensitivity, its power and the velocity of propagation of the explosion.

For the perchlorates the sensitivity varies over a wide range, from the very sensitive simple alkyl esters to the much less sensitive triarylmethyl perchlorates. It is apparent that the sensitivity of these compounds is reduced in solution. This is partly due to a dilution effect and partly to a modification of the molecular structure from a purely covalent form to a more polar entity. The covalent perchlorate group is much less stable than the perchlorate ion, doubtlessly owing to the lack of symmetry in the former.

Once sufficient energy has been supplied to the perchlorate to initiate its decomposition, the rate of reaction is of the same order as that for other common explosives. Apart from the thermochemical aspects of explosions, it is the velocity of the decomposition that determines whether or not the reaction is explosive.

The power of the explosive is governed largely by the pressure of the gases produced in the decomposition. The position is especially favourable for the simpler alkyl perchlorates because the stoichiometry of the compounds means that almost complete oxidation of the organic residue can occur, *e.g.*—



The products are completely gaseous, so a large increase in volume (or pressure at constant volume) occurs. The power is increased further by the expansion of the gases owing to the high temperature of the explosion, frequently several thousand degrees centigrade.

These facts are important because they give an indication of the methods that should be employed for the destruction of organic matter with perchloric acid. It is clear that these must depend on the prevention of appreciable concentrations of organic perchlorates, or of anhydrous perchloric acid, being formed during the destructions. This can be achieved by performing a preliminary destruction with nitric acid or nitric acid-sulphuric acid, followed by cautious dropwise addition of perchloric acid to the mixture. The latter should contain a fair excess of nitric or sulphuric acid, or both, although it should be noted that the use of sulphuric acid can lead to the formation of anhydrous perchloric acid. The temperature should be high enough for the perchloric acid to react as fast as it is added. It is not recommended that destructions of organic material be carried out in perchloric acid alone. Materials, such as machine oils and greases, that do not dissolve readily in the oxidising medium are liable to cause most trouble with perchloric acid (*cf.* Zahn⁴; Sutcliffe¹²⁰). Under these conditions it is difficult to avoid localised heat effects.

This represents a reasonably safe general method for carrying out destructions, and is essentially due to Kahane, who has worked out methods for estimating B, I, S, N, P, As, Si, and the metals (Kahane *et al.*^{123,124,125,126}). There are many examples in the literature, where various techniques for using perchloric acid have been described for the determination of trace elements in materials of plant and animal origin.¹²⁷⁻¹⁴⁰ Others have been mentioned in a recent critical review of the subject (Middleton and Stuckey¹⁴¹). The relative advantages, or otherwise, of these modifications might well be considered in the light of the present discussion, taking into account the various mishaps that have been recorded. Treatment of tervalent antimony (Hillebrand and Lundell⁹⁴) or bismuth compounds (Nicholson and Reedy¹⁴²) with perchloric acid can be very hazardous.

The use of perchloric acid for Kjeldahl estimations of nitrogen has the advantage of speed, but there is some uncertainty about the accuracy of the results (Bradstreet¹⁴³).

Recently, the whole question of the wet-ashing of organic matter has been considered in an admirable paper by Smith.¹⁴⁴ The procedures used have been called "liquid-fire reactions" because they result in the complete oxidation of organic matter to carbon dioxide and water at relatively low temperatures (100° to 235° C). The method has many advantages over dry-ashing procedures at high temperatures. A wide range of materials has been considered and it has been found that often the decomposition proceeds smoothly if catalysed by vanadium. The mechanism of the decompositions is described in terms of the oxidation potentials of the various oxidising systems used.

It will be apparent that many interesting aspects of the perchlorates have had to be omitted from this review, *e.g.*, nitrosium and nitronium perchlorates, the perchlorates of the halogens and of the metals. However, mention must be made of magnesium perchlorate ("anhydrone") (Willard and Smith¹⁴⁵) and its trihydrate ("dehydrite") (Smith, Brown and Ross¹⁴⁶), which are frequently used as drying agents. If these are used for drying organic liquids, the origin of the drying agent should be determined, because, in the process for its preparation, traces of perchloric acid may have been retained in the salt. Explosions have been known to occur when these compounds are used, possibly owing to the formation of free perchloric acid, or perchloric esters, in the system (Stross and Zimmerman¹⁴⁷). These substances are not recommended for drying such easily polymerisable materials as styrene (Lilley and Foster¹⁴⁸). It should also be pointed out that many metallic perchlorate-solvent complexes are explosive in the dry state, *e.g.*, the silver perchlorate-benzene complex (Brinkley¹⁴⁹).

An attempt has been made to give an outline of some of the fundamental aspects of the chemistry of perchloric acid, rather than to lay down rules as to when the acid can be used without hazard. At present we feel that this cannot justifiably be done, but that each case must be considered in the light of the above discussion and in the light of experiment. We do not underrate the hazards involved, but there is no doubt that danger can often be avoided if careful consideration is given to experimental conditions and to subsequent operations.

Undoubtedly, perchloric acid will become another useful reagent in the chemist's armoury, provided that familiarity never breeds contempt.

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QUEEN ELIZABETH COLLEGE (UNIVERSITY OF LONDON)
CAMPDEN HILL ROAD, W.8

July 23rd, 1954