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The Synthesis and Properties of Covalent Organic Perchlorates

N.S.Zefirov, V.V.Zhdankin, and A.S.Koz'min

The review is devoted to the chemistry of perchloric acid esters—a relatively little investigated class of compounds with exceptionally interesting properties. Data on the methods of synthesis and reactivities of covalent organic perchlorates are described systematically and surveyed.
The bibliography includes 141 references.

CONTENTS

I. INTRODUCTION

During the last 30 years, there has been a sharp increase of interest in perchloric acid and its derivatives. Inorganic and organic compositions based on perchlorates have found extensive applications as rocket fuel and explosives, industrial catalysts, drying agents, accumulator electrolytes, etc.[1] Perchloric acid and perchlorates have come to be widely used in scientific research in analytical, physical, and organic chemistry. The growing interest in perchlorates has been expressed in a fairly large number of publications appearing annually in the periodical literature. However, the vast majority of these studies are concerned with perchlorates having ionic structures—inorganic and organic salts of perchloric acid. Although the first covalent perchorate, ethyl perchlorate, was obtained as early as 1841,[2] the chemistry of compounds of this class has developed very slowly until recently; thus at best 1 – 2 pages have been devoted to them in the two existing reviews[3,4] and monographs.[1,5]

The reason for this is evident—perchloric acid esters are mostly relatively unstable and extremely explosive substances, which makes working with them very difficult. However, spectroscopic identification methods which have been developed during the last 20 years as well as the technique involving experiments at low temperatures with microamounts of substances have made it possible to reduce the risk in studies in this field to a minimum. Furthermore, there has been a growth of interest in the possible practical applications of covalent organic perchlorates as alkylating agents[6] and polymerisation catalysts.[7-10] These factors as well as the evident theoretical interest which the highly reactive covalent perchlorates represent has led many investigators in recent years to search for new ways of synthesising perchloric acid esters. Among the advances in this field, we may mention the discovery of the phenomenon of the competitive binding of nucleofugitive anions, including ClO_4^-, in carbonium ion processes which have made it possible to extend sharply the range of perchlorates synthesised.

The synthesis of a large set of relatively stable covalent perchlorates, namely arenesulphonylmethyl perchlorates,[11] perfluoroalkyl perchlorates,[12,13] certain skeletal perchlorates,[14-17] as well as silyl perchlorates,[18] may be mentioned as a considerable advance in the chemistry of perchlorates during the last 10 – 15 years, which has allowed a more thorough investigation of the reactivity of compounds of this interesting class. Furthermore, the development of kinetic measurement techniques made it possible to investigate the detailed mechanisms of the reactions of a series of highly reactive unstable perchlorates.[19-22] All these factors have made it urgently necessary to carry out an exhaustive survey of the literature data on covalent perchlorates and to analyse in detail both the results obtained and the prospects for the development of this branch of organic chemistry. The present review is devoted to this problem; it covers the entire available literature on the synthesis and properties of covalent perchlorates up to 1986 and is the first exhaustive survey of this field.

II. METHODS OF SYNTHESIS

1. General Principles of the Synthesis of Perchloric Acid Esters

One of the simplest covalent perchlorates—ethyl perchlorate—has been obtained by distillation from a concentrated solution of the barium salts of ethylsulphuric and perchloric acid:

$$Ba(RSO_4)_2 + Ba(ClO_4)_2 \rightarrow 2ROClO_3 + 2BaSO_4,$$
$$R{=}CH_3,\ C_2H_5,\ n\text{-}C_3H_7.$$

The possibilities of this method for the synthesis of methyl, ethyl, and propyl perchlorates were later investigated;[23] in particular, the optimum temperature range for these reactions was discovered (170 – 200 °C). Despite the appreciable danger involved,[3,23] this method was until 1936 virtually the only procedure for the preparation of lower alkyl perchlorates.[23,24]

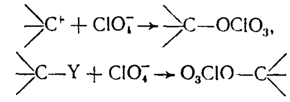
Progress in the synthesis of perchloric acid esters has been associated both with the introduction into practical organic synthesis of new inorganic reagents such as perchloric acid, chlorine pentoxide, silver perchlorate, and halogen perchlorates, and with a deeper understanding of the problem of nucleophilic reactivity as a whole.

Any ester of an inorganic acid ROX can be obtained, in principle, in two general ways. The first is based on the reaction of alcohols or their derivatives with the anhydride or halide of the given inorganic acid. In this method of synthesis of the inorganic acid ester, an oxygen – element bond is formed. When applied to covalent perchlorates, the method reduces to the reaction of alcohols and their derivatives with chlorine pentoxide or perchloryl fluoride:

$$ROH + Cl_2O_7 \rightarrow ROClO_3 + HClO_4,$$
$$ROH + FClO_3 \rightarrow ROClO_3 + HF.$$

At the present time, these reactions have been investigated in fair detail and will be examined below. On the whole, this is a fairly acceptable synthetic method, limited solely by the explosive properties of the reagents used, in particular, chlorine pentoxide.

The second general method of synthesis of esters of the type ROX is based on reactions in which the OX^- anion plays the role of the nucleophile attacking the electrophilic carbon atom; an oxygen–carbon bond is formed in this method of synthesis. When applied to the synthesis of covalent perchlorates, this means the use of the perchlorate anion ClO_4^- as the nucleophile:



The development of this approach was significantly restricted by the idea which arose at the beginning of the 1970s that the perchlorate anion has no nucleophilic properties. Indeed, attempts to measure the parameters of the nucleophilicity of ClO_4^- within the framework of the generally employed Swain–Scott[25] and Ritchie[26,27] scales were unsuccessful and estimates in terms of the two-parameter Edwards scale[28] provided grounds for the assumption that this anion is an ultra-weak nucleophile. This view is well reflected in the familiar textbook of Roberts and Caserio,[29] in which lithium perchlorate, a source of the perchlorate anion, is defined as a "non-nucleophilic substance". It is not fortuitous that perchloric acid salts, such as lithium perchlorate, are usually employed in connection with the study of salt effects, because these salts do not affect the course of the reaction by binding to the intermediate carbonium ion.[30–33]

It was believed previously that the covalent binding of the perchlorate anion, leading to covalent perchlorates, is possible only under specially created conditions: in the complete absence of other nucleophilic species and in media with a low polarity. On this basis, a number of methods were developed for the synthesis of covalent perchlorates, for example, by the reaction of alkyl halides with silver perchlorate or by the addition of halogen perchlorate to perfluoro-olefins (see below). A limitation of all these methods was the necessity to use exceptionally explosive or expensive reagents such as halogen perchlorates and silver perchlorate.

However, in recent years the authors of the present review found unexpectedly that the perchlorate ion can manifest nucleophilic properties also in the presence of extraneous nucleophiles (halide ions, AcO^-, AcOH, etc.).[14,15,34–36] This discovery (which applies also to other nucleofugitive anions as well as ClO_4^-—triflate, fluorosulphate, toluene-*p*-sulphonate, methanesulphonate, etc.[36]) made it possible to devise a series of new convenient methods of synthesis of covalent perchlorates having different structures. The methods developed are based on a wide range of carbonium ion processes such as electrophilic addition to olefins,[14,15,34–36] opening of epoxide rings,[36–40] deamination of amines,[34,41] chlorination of sulphides,[42] deoxygenation of alcohols by treatment with sulphur and chlorine,[43] oxidative substitution of iodine in alkyl iodides,[44,45] and the interaction of aryliodoso-derivatives with olefins.[46–48] Alkali metal perchlorates, which are safe to handle and are readily available, are used as the reagents in all these cases.

In conclusion of this Section, we may note that in the description below the data will be grouped in terms of the types of initial compounds rather than the reaction mechanisms; this arrangement of the material is dictated both by the synthetic bias of the present review and by the extremely scanty experimental data on the kinetics and mechanisms of the synthesis of covalent perchlorates.

2. Synthesis From Alcohols and Ethers

The synthetic possibilities of the reactions of alcohols with perchloric acid have been investigated in fair detail. The explosive character of the interaction of anhydrous perchloric acid with absolute ethanol was reported as early as 1936.[23] However, the reactions of polyhydric alcohols with perchloric acid take place more quietly and can be used for the preparative synthesis of perchloric acid mono- and poly-esters. Thus the esters of perchloric acid with ethylene glycol, glycerol, and pentaerythritol have been obtained by the direct interaction of the hydroxy-compounds with anhydrous perchloric acid, which plays the role of a powerful dehydrating agent in this reaction, forming a monohydrate.[49] The esterification was carried out by the cautious addition of the alcohol to an excess of perchloric acid at -78 °C, the mixture being subsequently maintained at 60–80 °C for 20–40 min. The isolation of the esterification products presented a special problem. It has been reported[49] that, when the reaction mixture is diluted directly with water, "enormously powerful explosions" take place, which are apparently a consequence of the very rapid heating on hydration of perchloric acid. This risk was avoided by diluting the reaction mixture initially with 70% perchloric acid. The subsequent addition of a large amount of water causes the precipitation of a deposit of the organic perchlorate in the form of a heavy oil (density in excess of 1.7) or flakes (in the case of pentaerythritol). The authors[49] had to design a special apparatus for the extraction of the perchlorates with ether because powerful explosions occurred in the usual separating funnel when the ethereal solution entered the ground joints.

A modification of the esterification of alcohols with perchloric acid was subsequently developed.[50] Here the reagent employed was a mixture comprising 70% of perchloric acid, concentrated sulphuric acid, and oleum or a solution of an alkali metal perchlorate in 96% sulphuric acid. The alcohol is added slowly to a vigorously stirred emulsion of the acid reagents with an inert organic solvent at a temperature between -10° and 25 °C. The rapidly formed covalent perchlorate is concentrated in the organic phase. The method[50] is suitable only for the synthesis of secondary perchlorates from the corresponding alcohols (yield 70–90%), whilst primary alcohols react very slowly with formation of isomeric secondary perchlorates. The reaction mechanism apparently involves the preliminary formation of alkyl sulphates, the generation of a carbonium ion, possible isomersiation, and binding to the perchlorate anion. The carbonium ion character of the process has been confirmed, in particular, by the formation of an identical 1:1 mixture of 2- and 3-hexyl perchlorates when the reaction was carried out with both 2-hexanol and 3-hexanol.

A convenient method of synthesis of covalent perchlorates by the interaction of alcohols with chlorine heptoxide has been proposed:[51]

$$ROH + O_3ClOClO_3 \rightarrow ROClO_3 + HClO_4.$$

Chlorine heptoxide was used in the form of a relatively safe solution in carbon tetrachloride[52] and the perchloric acid produced in the reaction was bound with sodium sulphate.

One of the attractive features of this reaction is the formation of perchlorates exclusively with a non-rearranged structure, on the basis of which it has been concluded[51] that the C–O bond is really not involved in this reaction. The method yields best results for primary alcohols and diols, while in the reactions with secondary alcohols the corresponding ketones are formed as side products (8–9%) together with the perchlorates. The wide variety of structures and the yields of the covalent perchlorates in the reactions investigated are demonstrated by the data in Table 1. Baum and Beard[51] noted that they were unable to obtain t-butyl perchlorate, apparently because of the instability of this product. On the other hand, perfluoro-t-butyl perchlorate proved to be entirely stable and was obtained in 33% yield by the reaction of sodium alkoxide with chlorine pentoxide:[51]

$$(CF_3)_3CONa + Cl_2O_7 \rightarrow (CF_3)_3COClO_3 + NaClO_4.$$

Apart from the alcohols themselves, their alkoxides can also be used as starting materials, the role of the reagent being usually assumed in this instance by perchloryl fluoride:[53]

$$RO^-M^+ + FClO_3 \rightarrow ROClO_3 + MF,$$
$$M{=}Na,\ (NH_2)_3C.$$

Table 1. The yields of covalent perchlorates in the reactions of alcohols with chlorine heptoxide in carbon tetrachloride (according to Baum and Beard's data[51]).

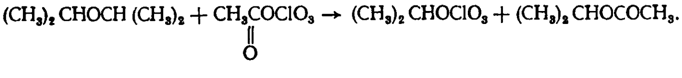
Initial alcohol	Perchlorate obtained	Yield, %
CH_3OH	CH_3OClO_3	42
C_2H_5OH	$C_2H_5OClO_3$	56
$n\text{-}C_3H_7OH$	$n\text{-}C_3H_7OClO_3$	73
$n\text{-}C_4H_9OH$	$n\text{-}C_4H_9OClO_3$	71
$n\text{-}C_5H_{11}OH$	$n\text{-}C_5H_{11}OClO_3$	63
$n\text{-}C_6H_{13}OH$	$n\text{-}C_6H_{13}OClO_3$	58
$HOCH_2CH_2OH$	$O_3ClOCH_2OClO_3$	60
$HOCH_2(CH_2)_2CH_2OH$	$O_3ClOCH_2(CH_2)_2CH_2OClO_3$	38
CF_3CH_2OH	$CF_3CH_2OClO_3$	55
$CH_3C(NO_2)_2CH_2OH$	$CH_3C(NO_2)_2CH_2OClO_3$	67
$FC(NO_2)_2CH_2OH$	$FC(NO_2)_2CH_2OClO_3$	60
$FC(NO_2)_2CH_2OCH_2CH_2OH$	$FC(NO_2)_2CH_2OCH_2CH_2OClO_3$	43
$CH_2{=}CHCH_2OH$	$CH_2{=}CHCH_2OClO_3$	48
$HC{\equiv}CCH_2OH$	$HC{\equiv}CCH_2OClO_3$	43
$CH_3CHOHCH_3$	$CH_3CH(OClO_3)CH_3$	48
$CH_3CHOH(CH_2)_3CH_3$	$CH_3CH(OClO_3)(CH_2)_3CH_3$	62
$CH_3CH_2CHOH(CH_2)_2CH_3$	$CH_3CH_2CH(OClO_3)(CH_2)_2CH_3$	53

Alcohols can serve as the starting materials in the synthesis of covalent perchlorates in yet another reaction, which is a deoxygenation process. In this reaction, developed by the authors of the present review,[43] sulphur, chlorine, pyridine, and lithium perchlorate were used as the reagents. The possibility of the formation of covalent perchlorates is because the alcohols are intially converted into chlorosulphenates by the sulphur dichloride arising as an intermediate and these then generate dichloroalkoxysulphonium ions, which undergo nucleophilic substitution by the perchlorate anion:

$$ROH \xrightarrow{\overset{S+Cl_2}{\downarrow}\atop SCl_2} [ROSCl] \xrightarrow{Cl_2} \underset{Cl^-}{[RO\overset{+}{S}Cl_2]} \xrightarrow{ClO_4^-} ROClO_3,$$

$$R{=}C_8H_{17},\ \text{2-chlorocyclohexyl}.$$

The reactions of ethers with chlorine heptoxide and acyl perchlorates have been investigated.[54] Acyl perchlorates, obtained by the reaction of acyl chlorides with silver perchlorates (see below) in carbon tetrachloride, cleave secondary ethers with formation of a mixture of secondary alkyl perchlorates and alkyl acetates:

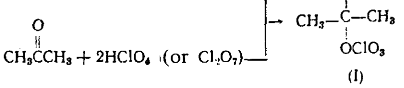


$$(CH_3)_2CHOCH(CH_3)_2 + CH_3\underset{\underset{O}{\|}}{C}OClO_3 \rightarrow (CH_3)_2CHOClO_3 + (CH_3)_2CHOCOCH_3.$$

Primary ethers do not enter into this reaction. Like acetyl perchlorate, benzoyl and *NN*-diethylcarbamoyl perchlorates react with ethers.[54]

In contrast to acyl perchlorates, chlorine heptoxide is capable of cleaving not only secondary but also primary ethers.[54] For example, diethyl ether reacts slowly with chlorine heptoxide, forming ethyl perchlorate.[54]

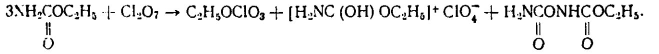
The main product of the reaction of diisopropyl ether with chlorine heptoxide is the geminal diperchlorate (I),[54] which can also be obtained by the reaction of acetone with chlorine heptoxide[55] or with anhydrous perchloric acid:[56]



$$\left.\begin{array}{l}(CH_3)_2CHOCH(CH_3)_2 + Cl_2O_7\\ CH_3\overset{\overset{O}{\|}}{C}CH_3 + 2HClO_4\ (\text{or } Cl_2O_7)\end{array}\right] \rightarrow CH_3-\underset{\underset{OClO_3}{|}}{\overset{\overset{OClO_3}{|}}{C}}-CH_3\ .$$

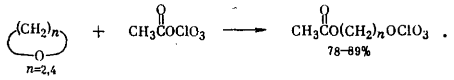
(I)

Esters can apparently also be cleaved by chlorine heptoxide with formation of covalent perchlorates. A single reaction of this type, resulting in the formation of ethyl perchlorate, has been described in the literature[57] (in relation to ethyl carbamate):

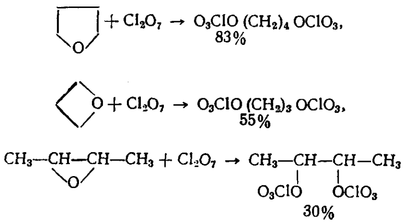


$$3NH_2\underset{\underset{O}{\|}}{C}OC_2H_5 + Cl_2O_7 \rightarrow C_2H_5OClO_3 + [H_2NC(OH)OC_2H_5]^+ClO_4^- + H_2N\underset{\underset{O}{\|}}{C}NH\underset{\underset{O}{\|}}{C}OC_2H_5.$$

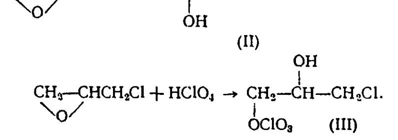
Cyclic ethers, including epoxides, can also be used as the starting compounds for the synthesis of organic perchlorates. It has been suggested that[54] they be cleaved with acyl perchlorates and chlorine heptoxide. For example, the reactions of acetyl perchlorate with tetrahydrofuran and epoxyethane take place at 0 °C with formation of the corresponding αω-acetoxyperchlorates:



Analogous reactions with chlorine heptoxide[47] lead to αω-diperchlorates:



Acid cleavage of epoxides can also be used for the synthesis of covalent perchlorates. As early as the beginning of the XXth century, Hofmann et al.[58] investigated the reactions of epoxyethane and epichlorohydrin with concentrated (70%) perchloric acid and obtained the explosive compounds (II) and (III):

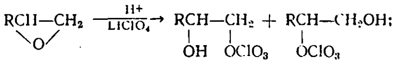


(II)

(III)

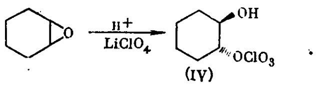
The kinetics of the opening of the epoxide rings with perchloric acid[59] or other acids in the presence of lithium perchlorate[60] have been investigated in detail. Strong evidence has been obtained in support of the carbonium ion character of the intermediates in these processes,[59] but the formation of covalent perchlorates was not detected in the above studies.[59,60]

The authors of the present review developed a preparative method for the synthesis of covalent perchlorates in reactions involving coupled acid opening of epoxide rings in the presence of perchloric acid salts.[37,40] Epoxyethane, epoxypropane, epoxycyclohexane, and also the epoxy-derivative (VII) of tricyclo[4.2.2.0^{2,5}]decane were chosen as the objects of study. Covalent perchlorates were obtained in all cases by treating these compounds with an acid (acetic, sulphuric, or perchloric) in the presence of lithium perchlorate in ether or ethyl acetate. The β-hydroxy-perchlorates (IV)–(VI) are formed under these conditions from the epoxy-derivatives obtained from alkenes and cyclohexene:[37,40]



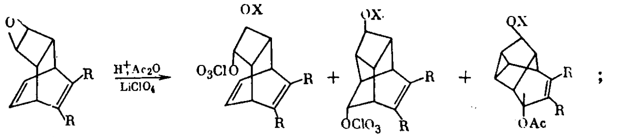
(IV) (V)

$R=H, CH_3$.



(IV)

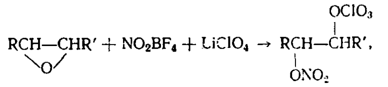
The acid cleavage of the skeletal epoxide (VII) in the presence of lithium perchlorate resulted in the formation of a complex mixture of products including the covalent perchlorates (VIII) and (IX):[38,39]



(VII) (VIII) (IX) (X)

$R=CO_2CH_3$; $X=H, OAc$.

When the epoxide rings are opened not with an acid but with nitronium fluoroborate in the presence of lithium perchlorate in an inert solvent, the formation of β-nitratoalkyl perchlorate in high yields is observed:[37]



$R=R'=H$; $R=CH_3$, $R'=H$; $RR'=-(CH_2)_4-$.

3. Synthesis From Alkyl Halides

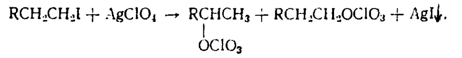
During recent years, the method of synthesis of alkyl perchlorates by the exchange reaction of alkyl halides with silver perchlorate in an organic solvent has come to be most widely used:

$$RX + AgClO_4 \rightarrow ROClO_3 + AgX\downarrow.$$

Anhydrous silver perchlorate is readily soluble in many organic solvents (the solubility of $AgClO_4$ in 100 g of the solvent is 5.3 g in benzene and 101 g in toluene[1]); when an equivalent amount of an alkyl halide is added to such a solution, the rapid formation of a silver halide precipitate is observed, and its rapid removal can produce a solution containing only the alkyl perchlorate. Dilute solutions of alkyl perchlorates are usually safe to handle.

The reactions of alkyl halides with silver perchlorate in a wide variety of solvents have been investigated. It has been shown that ethanol,[24] acetonitrile,[61] and anisole[62] are relatively unsuitable for the synthesis of alkyl perchlorates, which are excellent alkylating agents[4] and readily react with these solvents. The use of chlorohydrocarbon solvents, for example, carbon tetrachloride, which may react with silver perchlorate to form the explosive trichloromethyl perchlorate,[63] is not recommended either. In practice, diethyl ether,[23] dioxan,[64] nitromethane,[65,66] pentane,[67] and benzene[68] are used for the preparative synthesis of alkyl perchlorates.

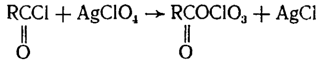
Alkyl perchlorates are usually obtained from alkyl iodides,[6,67,69,70] although the reactions of alkyl bromides with silver perchlorate have also been studied.[23,68] A series of n-alkyl perchlorates have been prepared by the reaction of C_5-C_8 alkyl iodides with silver perchlorate in pentane in 90–95% yields.[67] However, recent studies[6,51] have cast doubt on the result of this reaction. It was found that, when the reaction of alkyl iodides is carried out in the majority of solvents, with the exception of benzene, a mixture of primary and secondary perchlorates is formed:



$$RCH_2CH_2I + AgClO_4 \rightarrow \underset{\displaystyle OClO_3}{\underset{|}{RCHCH_3}} + RCH_2CH_2OClO_3 + AgI\downarrow.$$

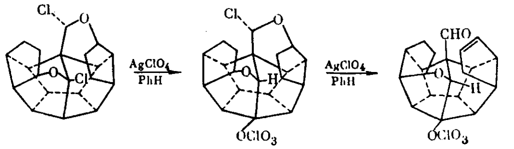
For example, this reaction in carbon tetrachloride affords a 1:1 mixture of primary and secondary perchlorates;[6] on the other hand, the reaction of primary alkyl iodides with silver perchlorate in benzene gives a 90% yield of primary alkyl perchlorates exclusively.[6]

The reaction of halogeno-derivatives with silver perchlorate has also uses other than the synthesis of alkyl perchlorates. It has been shown by indirect chemical methods[69,71] and also by ^1H NMR [51] that allyl and benzyl perchlorates, as well as acyl perchlorates,[54] can be obtained analogously from acyl chlorides and silver perchlorate:



$$\underset{\displaystyle O}{\underset{\|}{RCCl}} + AgClO_4 \rightarrow \underset{\displaystyle O}{\underset{\|}{RCOClO_3}} + AgCl\downarrow.$$

Covalent silyl perchlorates[72,73] and certain skeletal perchlorates of the norbornane[74] and adamantane[19,20] series have been synthesised by the reactions of the corresponding halides with silver perchlorate. The skeletal covalent perchlorates (XII) and (XIII) have been synthesised by treating the dichloride (XI) (heterocyclic analogue of trisecododecahedrane) with silver perchlorate in benzene:[16,17]



(XI) (XII) (XIII)

It has been noted[16] that compound (XIII) is the first example of a stable tertiary covalent perchlorate.

The mechanism of the reaction of alkyl halides with silver perchlorate has been investigated quite vigorously. As early as 1940, the kinetics of the reaction of methyl iodide with silver perchlorate were studied in acetic acid, acetone, ethanol, benzene, ethyl acetate, and 50% aqueous ethanol.[70] It was found that the order of this reaction depends on the initial concentration of the reactants and is on average 2.5; the activation energy is 11–13 kcal. The authors[70] established that the rate of reaction is influenced by the excess colloidal silver iodide, which is not removed from the solution for a long time. Further studies[65,66,68,75] showed that the reaction of alkyl iodides with silver perchlorates proceeds via the formation of the ion-pair complex (XIV), which slowly decomposes in a solvent with a low dielectric constant to a covalent perchlorate and silver halide:

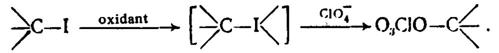
$$RX + AgClO_4 \rightleftarrows [ClO_4^-R^+X^-Ag^+] \rightarrow \text{products.}$$
(XIV)

The reaction of 2-octyl bromide with silver perchlorate in nucleophilic (acetonitrile)[61] and non-nucleophilic (benzene)[68] solvents has been investigated. In both solvents, the reaction is of first order with respect to alkyl bromide and of variable order with respect to silver perchlorate. In acetonitrile, the reaction order with respect to silver perchlorate varies from 1 (at very low concentrations of the salt) to 2 (for 0.3 M $AgClO_4$); in benzene, the order with respect to silver perchlorate varies from 1.5 to 2. These results are consistent with earlier data.[70] It has also been observed[61,68] that, at low silver perchlorate concentrations, small amounts of added tetrabutylammonium perchlorate have a considerable catalytic effect; furthermore, the formation of olefins as side products is reduced in the presence of the ionic perchlorate. The catalytic action of the salt has been explained[61] by the nucleophilic involvement of the perchlorate anion in the rate-limiting stage of the reaction. The reaction with the optically active 2-octyl bromide in benzene leads to the formation of a 2:3 mixture of the enantiomeric 2-octyl perchlorates, the product with the inverted configuration predominating.[68] This result is independent of the silver perchlorate concentration and the addition of tetrabutylammonium perchlorate. It has been noted[68] that the reaction of 2-octyl bromide with silver perchlorate in benzene is much faster than in acetonitrile as a consequence of the formation of a strong complex between the Ag^+ cation and acetonitrile.

Since the ion-pair association and the tendency towards the formation of ionic aggregates by silver perchlorate greatly complicate the study of the kinetics of the reactions with alkyl halides in benzene, a solvent with a high dielectric constant (nitromethane), in which silver perchlorate is almost wholly ionised, was used.[65,66] The reaction of methyl iodide with silver perchlorate in nitromethane takes place with formation of 80% of methyl perchlorate and 20% of a side product of unknown composition, which precipitates together with silver iodide as a red amorphous deposit.[66] As for the other solvents, the complex (XIV) is formed in the first stage of the process and then decomposes rapidly, in several stages, into the final reaction products. The same mechanism has been proposed[65] for the reaction of neopentyl iodide with silver perchlorate in nitromethane, but the rate of this reaction is 33 times greater than that of the analogous reaction of methyl iodide.

The reaction of alkyl halides with silver perchlorate has found a practical application, mainly for the synthesis of methyl perchlorate, which is a powerful methylating agent.[76–78] A disadvantage of this method of synthesis of covalent perchlorates is the necessity to use the expensive and explosive anhydrous silver perchlorate.[1] The possibility of a rearrangement when primary alkyl iodides are used also diminishes the synthetic value of the reaction.[6]

The methods of synthesis of covalent perchlorates from alkyl iodides based on the oxidative iodine elimination reactions are partly free from these disadvantages. The central feature of these processes consists in the oxidation of the iodine atom in alkyl iodides to the tervalent state by various reagents (halogens,[79–81] peracids,[82] and a wide range of inorganic oxidants[83–85]) with formation of intermediates of type (XV). The iodine atom in the +3 oxidation state exhibits the properties of an exceptionally effective leaving group and can be readily substituted by the nucleophiles present,[79,82] including perchlorate anions:[36,44,45,86,87]



(XV)

Inorganic reagents can be represented in this reaction by a pair of substances, namely the oxidant – perchlorate anion-donor pair,[36,44,45] or by a single substance such as chlorine heptoxide,[87] a halogen perchlorate,[12,86,77] or μ-oxodiiodosodiphenyl diperchlorate.[89]

Chlorine[90] and bromine[91] perchlorates have been used[12,86,88] to synthesise perfluorinated alkyl perchlorates. These reagents were first obtained at the beginning of the 1970s in 70 – 95% yield by keeping caesium perchlorate or nitronium perchlorate with the fluorosulphate of the corresponding halogen for a long time at –45 °C:[90,91]

$$MClO_4 + XSO_3F \rightarrow MSO_3F + XOClO_3,$$
$$M{=}Cs,\ NO_2;\ X{=}Cl,\ Br.$$

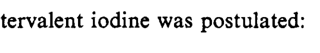
The reactions of lower perfluorinated alkyl iodides with chlorine perchlorate take place smoothly at temperatures between –200° and –45 °C with formation of stable covalent perfluoroalkyl perchlorates (XVII) in 95 – 99% yield:[12,86,88]

$$\underset{}{C_nF_{2n+1}I} + 2ClOClO_3 \xrightarrow[-Cl_2]{} \underset{(XVI)}{C_nF_{2n+1}I\,(ClO_4)_2} \rightarrow \underset{(XVII)}{C_nF_{2n+1}OClO_3} + [IClO_4].$$

Compound (XVI), formed in the first stage of the reaction of trifluoromethyl iodide or pentafluoroethyl iodide with fluorine perchlorate, cannot be isolated and the final products of the reaction are gaseous perfluoroalkyl perchlorates, chlorine, and the products of the decomposition of the unstable iodine perchlorate. However, in other cases it is possible to obtain crystalline intermediates stable at room temperature, for example, $(CF_3)_2CFI(ClO_4)_2$ (m.p. 71 to 73 °C) and $C_7F_{15}I(ClO_4)_2$ (m.p. 56 – 78 °C), which decompose on moderate heating (below 100 °C) with formation of the corresponding covalent perchlorate.[12]

Bromine perchlorate reacts analogously with perfluoroalkyl iodide, but the yields of perfluoroalkyl perchlorates are somewhat lower in this case.[12] The replacement of perfluoroalkyl iodides by the bromides also entails a decrease in the yields of covalent perchlorates. The most stable halogen perchlorate, namely fluorine perchlorate, gives rise to only trace amounts of covalent perchlorates in its reaction with perfluoroalkyl iodides.[13] We may note that halogen perchlorates are extremely explosive even at temperatures of about –200 °C and rapidly decompose at room temperature.[90,91]

The studies of Schack and co-workers[86,88] stimulated the investigation of the reactions of alkyl iodides with chlorine heptoxide. Thus it has been found[87] that the main products of these reactions are covalent perchlorates and the formation of the intermediate (XVIII) with tervalent iodine was postulated:



$$R{-}I + Cl_2O_7 \rightarrow \underset{(XVIII)}{\left[R{-}I{\genfrac{}{}{0pt}{}{ClO_3}{OClO_3}}\right]} \rightarrow ROClO_3 + \underset{(XIX)}{[IClO_3]}.$$

The unstable iodine chlorate (XIX) formed decomposes with formation of I_2O_5 and Cl_2O. The presence of halogen oxides and mixed iodine and chlorine oxides in the reaction mixture leads to the formation of esters and ethers as side products. For example, 22% of ethyl acetate and trace amounts of diethyl ether are obtained together with ethyl perchlorate (63%) in the reaction of ethyl iodide with an excess of chlorine heptoxide at 0 °C:

$$C_2H_5I + Cl_2O_7 \rightarrow I_2O_5 + C_2H_5OClO_3 + CH_3\underset{\underset{O}{\|}}{C}OC_2H_5 + C_2H_5OC_2H_5.$$

The use of an equivalent amount of chlorine heptoxide lowers the yield of ethyl perchlorate and leads to a sharp increase in the content of diethylether in the reaction mixture (more than 20%).

In the course of the study of the phenomenon of the competitive binding of ultraweak nucleophiles in carbonium ion processes, the present authors investigated the possibility of the formation of covalent perchlorates in the oxidative decomposition of alkyl iodides.[44,45,89] The methods of synthesis of alkyl perchlorates developed are based on the oxidation of alkyl iodides in the presence of perchloric acid salts which in this case play the role of a reagent—a source of perchlorate anions:

$$CH_3(CH_2)_nI + M^+ClO_4^- \xrightarrow{[Ox]} CH_2(CH_2)_nOClO_3,$$
$$n = 0-5;\ M = Li,\ Bu_4N;\ [Ox] = m\text{-}ClC_6H_4COOOH,$$
$$H_5IO_6,\ Cl_2,\ NO_2BF_4.$$

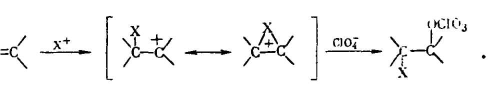
The reactions were performed by adding an oxidant [Ox], for example, chlorine, *m*-chloroperbenzoic acid, or iodic acid, to a solution of alkyl iodide in an aprotic solvent (ether, ethyl acetate, or chloroform) in the presence of 1 – 5 equivalents of lithium perchlorate or tetrabutylammonium perchlorate. Alkyl perchlorates were isolated in 50 – 70% yield by distillation or chromatography on a silica gel column. The geminal methylene diperchlorate (XX) was obtained for the first time by the oxidative deiodination of methylene iodide:[45]

$$CH_2I_2 + 2LiClO_4 + 2NO_2BF_4 \rightarrow \underset{(XX)}{CH_2(OClO_3)_2}.$$

The oxidation of organic iodides in the presence of sources of perchlorate anions is in our view one of the safest and most convenient methods of synthesis of covalent perchlorates of different types.

4. Synthesis From Olefins

The possibility of obtaining covalent perchlorates from olefins is associated with a two-stage mechanism of the electrophilic addition and generation of carbonium ion intermediates:



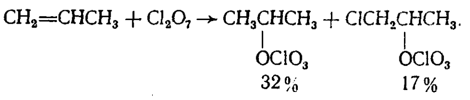
The addition of perchloric acid, chlorine heptoxide, and halogen perchlorate has been studied in special detail.[13,50,55,92–95] The studies of the reaction of but-2-ene with anhydrous perchloric acid in methylene chloride were some of the first in this field.[92] The organic perchlorate could not be isolated from the reaction mixture after treatment with water, but identification of 2-butanol and diisobutyl ether confirmed indirectly the formation of 2-butyl perchlorate in this reaction. The authors[92] also reported powerful explosions, which occurred when the butene was introduced into the perchloric acid solution.

The study of the reaction of *cis*-octadec-9-ene with 70% perchloric acid at 100 °C showed[93] that rapid migration of the double bond in the molecule is observed under these conditions. Octadecyl esters of perchloric acid are formed in the above reaction only in trace amounts (2%), while an olefin with a terminal double bond affords 14% of the perchlorate under the same conditions. The reaction of unsubstituted olefins with perchloric acid in the presence of oleum and an inert organic solvent (hexane, chlorobenzenes, etc.) has been studied in greater detail.[50,94] Higher yields of perchlorate (up to 100%) were obtained at reduced temperatuers (–10 °C); the increase to room temperature leads to a sharp reduction of the yields.[50]

Table 2. The yields of secondary alkyl perchlorates in the reactions of olefins with perchloric acid in the presence of a acid catalyst (H_2SO_4 + SO_3).[50]

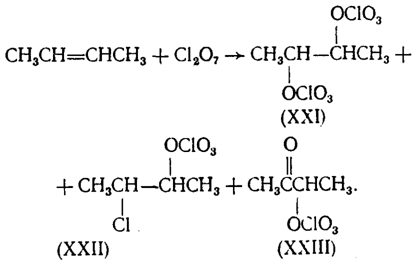
Olefin	Reaction product	Yield, %
Propene	$CH_3CH(OClO_3)CH_3$	96
Pent-1-ene	$CH_3CH(OClO_3)(CH_2)_2CH_3$	98
Hex-1-ene	$CH_3CH(OClO_3)(CH_2)_3CH_3$	99
Cyclohexene	$(CH_2)_5CHOClO_3$	89
Dec-1-ene	$CH_3CH(OClO_3)(CH_2)_7CH_3$	100
Octadec-1-ene	$CH_3CH(OClO_3)(CH_2)_{15}CH_3$	100
4-Phenylbut-1-ene	$PhCH_2CH_2CH(OClO_3)CH_3$	85
5-Methylhex-1-ene	$CH_3CH(CH_3)CH_2CH_2CH(OClO_3)CH_3$	76
Octa-1,7-diene	$CH_3CH(OClO_3)(CH_2)_4CH(OClO_3)CH_3$	85

In a study of the reactions of olefins with chlorine heptoxide in carbon tetrachloride, it was shown that they usually proceed with formation of a mixture of perchlorates, whose composition is determined by the structure of the olefin.[55] Thus the reaction of propene with chlorine heptoxide affords a mixture of 2-propyl and 1-chloropropyl perchlorates:



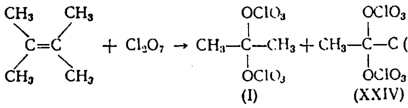
$$CH_2{=}CHCH_3 + Cl_2O_7 \rightarrow \underset{\underset{32\%}{OClO_3}}{\underset{|}{CH_3CHCH_3}} + \underset{\underset{17\%}{OClO_3}}{\underset{|}{ClCH_2CHCH_3}}.$$

Under these conditions, but-2-ene gives rise to the more complex mixture of products (XXI) – (XXIII), which is the same for the *cis*- and *trans*-olefins:



$$CH_3CH{=}CHCH_3 + Cl_2O_7 \rightarrow \underset{(XXI)}{CH_3\underset{OClO_3}{\underset{|}{C}}H-\overset{OClO_3}{\overset{|}{C}}HCH_3} +$$
$$+ \underset{(XXII)}{CH_3\underset{Cl}{\underset{|}{C}}H-\overset{OClO_3}{\overset{|}{C}}HCH_3} + \underset{(XXIII)}{CH_3\overset{O}{\overset{\|}{C}}\underset{OClO_3}{\underset{|}{C}}HCH_3}.$$

The reaction of tetramethylethylene with chlorine heptoxide leads to the formation of a mixture of the geminal diperchlorates (I) and (XXIV), which are insoluble in carbon tetrachloride:



$$(CH_3)_2C{=}C(CH_3)_2 + Cl_2O_7 \rightarrow \underset{(I)}{CH_3-\overset{OClO_3}{\underset{OClO_3}{C}}-CH_3} + \underset{(XXIV)}{CH_3-\overset{OClO_3}{\underset{OClO_3}{C}}-C(CH_3)_3}.$$

Olefins with electron-accepting substituents (1,1-difluoroethylene, allyl chloride) and ethylene virtually do not react with chlorine heptoxide, but the addition of small amounts of water catalyses the reaction and leads to acceptable yields of perchlorates, which are in this case the products of the addition of perchloric acid to the double bond:

$$CF_2{=}CH_2 + Cl_2O_7 \xrightarrow[CCl_4]{H_2O} \underset{76\%}{CH_3CF_2OClO_3},$$

The wide variety of products in the reactions of olefins with chlorine heptoxide is apparently due to the combination of oxidation-reduction processes and a series of secondary reactions.[55] For example, the formation of the diperchlorate (XXI) can be explained by the interaction of chlorine heptoxide with the epoxide formed when but-2-ene is oxidised.

The additon of halogen perchlorates to the double bond has been studied in relation to perfluorinated olefins.[13,95] The reactions of chlorine and bromine perchlorates with tetrafluoroethylene, perfluoropropene, chlorotrifluoroethylene, and other perhalogeno-olefins take place rapidly at temperatures below -70 °C and lead to perhalogenoalkyl perchlorates in high yields (90–100%).[95] Chlorine and bromine perchlorates add to perfluoropropene strictly regiospecifically with formation of products of only kind—the perchlorates (XXV), in accordance with the Markovnikov rule, which is strong evidence in support of a polar addition mechanism:

$$CF_3CF{=}CF_2 + XOClO_3 \rightarrow \underset{(XXV)}{CF_3CFXCF_2OClO_3}.$$

$$X{=}Cl,\ Br.$$

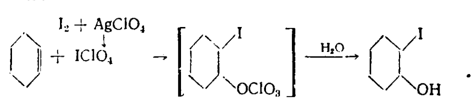
On the other hand, a mixture of isomers having the normal structure [compound (XXVI)] and the iso-structure [compound (XXVII)] is formed in the reaction of fluorine perchlorate with perfluoropropene:[13]

$$CF_3CF{=}CF_2 + FOClO_3 \rightarrow CF_3CF_2CF_2OClO_3 + CF_3\underset{\displaystyle OClO_3}{\underset{|}{C}}FCF_3.$$

(XXVI), 68% (XXVII), 32%

For this reaction, the authors[13] also proposed an ionic addition mechanism; the formation of the secondary perchlorate (XXVII) can be accounted for by the initial electrophilic attack by the oxygen atom on the carbon atom in the 2-position (the polarity of the F–O bond is probably the opposite of that of the Cl–O and Br–O bonds).

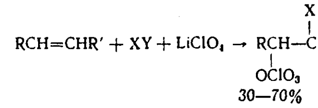
The addition of halogen perchlorates to unsaturated hydrocarbons has not been investigated. The only study on these lines[96] is at present only of historical interest. The authors[96] suggested that an ethereal solution of silver perchlorate and iodine contains iodine perchlorate and attempted to obtain 2-iodocyclohexyl perchlorate by treating cyclohexene with this solution:



(XXVIII)

However, the reaction product (XXVIII) proved to be unstable and the authors were able to isolate only 2-iodocyclohexanol after treating the reaction mixture with water. Here we may note that, according to the latest data,[12,97] iodine perchlorate is unstable and decomposes with formation of compounds of iodine in higher oxidation states even at temperatures below -50 °C. We therefore think that the explanation of the formation of compound (XXVIII) by the addition of $IClO_4$ to cyclohexene[96] is unlikely. An alternative mechanism may involve the coupled addition of iodine and the perchlorate anion to the double bond (see below).

In the course of a study of the competitive binding of the perchlorate anion in carbonium ion processes, we studied in detail the reactions involving the coupled electrophilic addition of perchlorate to olefins.[14,15,35,98–100] A whole series of such reactions can be used for the preparative synthesis of covalent perchlorates. For example, the reactions of unsubstituted olefins (ethylene, hept-1-ene, and cyclohexene) with halogens or nitronium fluoroborate in the presence of a (2–10)-fold excess of lithium perchlorate take place smoothly in an aprotic organic solvent (ether, ethyl acetate, methylene chloride) with formation of β-halogeno- or β-nitro-perchlorates.[35] The addition takes place in accordance with the Markovnikov rule:



$$RCH{=}CHR' + XY + LiClO_4 \rightarrow \underset{\displaystyle OClO_3}{RCH}{-}\overset{\displaystyle X}{CHR'},$$

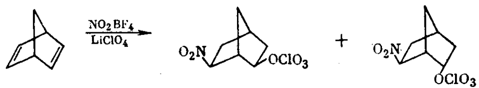
30—70%

$R{=}R'{=}H;\ R{=}C_5H_{11},\ R'{=}H;$

$RR'{=}(CH_2)_4;\ XY{=}Cl_2,\ Br_2,\ NO_2BF_4.$

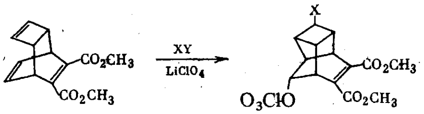
The reaction with cyclohexene leads to a mixture of the *cis*- and *trans*-substituted perchlorates.

The electrophilic perchlorate addition reactions have been investigated also for a series of skeletal olefins.[14,15,35] Thus norbornadiene reacts with nitronium fluoroborate and lithium perchlorate in ethyl acetate to form a mixture of the isomeric nitroperchlorates (XXIX) and (XXX) of the nortricyclene series (overall yield 72%):

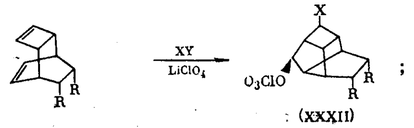


(XXIX) (XXX)

The reactions of skeletal olefins of the tricyclo[4.2.2.0^2,5]decane series with electrophiles and lithium perchlorate afford, together with other rearranged products, stable skeletal perchlorates,[14,15] for example:



(XXXI)



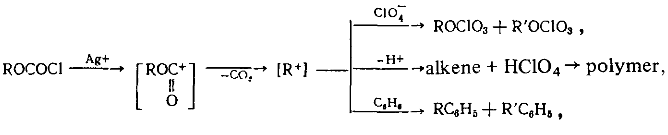
(XXXII)

R=CH₃,CO₂CH₃ .

The yields of the skeletal perchlorates (XXXI) and (XXXII) in these reactions reach 80%.

5. Synthesis of Covalent Perchlorates by Fragmentation Reactions

The next group of methods of synthesis of covalent perchlorates combines reactions involving the elimination of an electrically neutral species (N_2, CO_2, etc.) in the first stage. The reaction of alkyl chloroformates with silver perchlorate in benzene can be included among reactions of this type.[101] This reaction proceeds via a stage involving the elimination of a CO_2 molecule and leads to alkyl perchlorates together with benzene alkylation side products. In the course of the reaction, primary alkyl derivatives isomerise to secondary alkyl derivatives. The authors[101] proposed the following reaction mechanism:



$$ROCOCl \xrightarrow{Ag^+} \left[\begin{matrix} ROC^+ \\ \| \\ O \end{matrix}\right] \xrightarrow{-CO_2} [R^+] \left\{\begin{array}{l} \xrightarrow{ClO_4^-} ROClO_3 + R'OClO_3, \\ \xrightarrow{-H^+} \text{alkene} + HClO_4 \rightarrow \text{polymer}, \\ \xrightarrow{C_6H_6} RC_6H_5 + R'C_6H_5, \end{array}\right.$$

where R is a primary alkyl and R′ a secondary alkyl.

The yields of the perchlorates and benzene alkylation products in the reaction of chloroformate with a solution of silver perchlorate in benzene at 25 °C are given in Table 3. We may note that the low selectivity of this reaction limits significantly the scope of its use.

Table 3. The yields (%) of the products of the reactions of alkyl formates (ROCOCl) with silver perchlorate in benzene at 25 °C.[101]

R	$ROClO_3$	RC_6H_5	$R'OClO_3$	$R'C_6H_5$
CH_3	86	14	—	—
C_2H_5	47	37	—	—
n-C_3H_7	—	—	70*	10*
iso-C_3H_7	70	10	—	—
iso-C_4H_9	—	—	—	37**

*R′ = iso-C_3H_7; **R′ = t-C_4H_9.

The recently proposed[102,103] method of preparative nucleophilic substitution via "betylates"—salt-like compounds which are capable of readily eliminating the betaine fragment with formation of a covalent nucleophilic substitution product—is of undoubted synthetic value. In particular, the synthesis in 100% yield of 1-hexadecyl perchlorate via the betylate (XXXIII) by heating in toluene has been described:[102,103]

$$ROH \rightarrow \underset{(XXXIII)}{ROSO_2(CH_2)_2N^+(CH_3)_3\,ClO_4^-} \rightarrow ROClO_3 + {}^-O_3S(CH_2)_2\overset{+}{N}(CH_3)_3,$$
$$R{=}C_{16}H_{33}.$$

The reactions of aliphatic diazo-compounds with perchloric acid are accompanied by the evolution of nitrogen and also usually lead to covalent perchlorates. A reaction of this type was first carried out in a study[23] where methyl perchlorate was obtained by treating a solution of perchloric acid in ether with diazomethane:

$$CH_2N_2 + HClO_4 \rightarrow CH_3OClO_3 + N_2.$$

The authors[23] noted an extremely high risk of explosion in this method of synthesis of methyl perchlorate.

Dutch workers[11,104] used the reaction of diazosulphones with 70% perchloric acid in dichloroethane to synthesise covalent arenesulphonylmethyl perchlorates (XXXIV), whose yields reached 50%:

$$ArSO_2CHN_2 + HClO_4 \leftarrow \underset{(XXXIV)}{ArSO_2CH_2OClO_3} + N_2,$$
$$Ar = p\text{-}CH_3C_6H_4,\ C_6H_5CH_2,\ C_6H_5,\ p\text{-}ClC_6H_4,\ m\text{-}ClC_6H_4,\ p\text{-}NO_2C_6H_4.$$

The present authors[36,105] investigated the deamination of alkylamines with nitrous acid in the presence of lithium perchlorate. These processes, which also proceed via the intermediate formation of diazoalkanes, lead to covalent perchlorates as a result of the nucleophilic substitution of the diazo-group by the perchlorate anion. The reactions were carried out by adding various acids (for example, acetic or hydrochloric) to a mixture of alkylamines, sodium nitrite, and lithium perchlorate in an organic solvent (ether, ethyl acetate) or in water:

$$RNH_2 + NaNO_2 + HX + LiClO_4 \rightarrow ROClO_3,$$
$$R = n\text{-}C_4H_9,\ n\text{-}C_7H_{15},\ n\text{-}C_9H_{19};\ X = Cl,\ OAc.$$

Alkyl perchlorates were isolated from the reaction mixture in 30–40% yields.

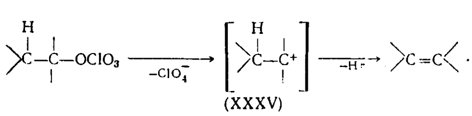
In conclusion of this Section, we emphasise yet again that all the traditional methods of synthesis of covalent perchlorates involve the risk of explosion to a greater or lesser extent. This risk is largely due to the nature of the inorganic reagents themselves—donors of the perchlorate group. Anhydrous silver perchlorate, which is most often used for this purpose, explodes even on friction.[1] The extremely high danger of the explosion of perchloric acid and chlorine heptoxide, especially on contact with organic solvents, is generally known. Fluorine, chlorine, and bromine perchlorates are unstable and extremely explosive at any temperatures and in any state.[90,91] On the other hand, the methods of synthesis of covalent perchlorates developed by the present authors[14,15,34,48,89,98–100] are more acceptable for practical use, since the reagents in these reactions are the lithium or alkylammonium salts of perchloric acid, which are safe to handle.

III. PROPERTIES

1. Physicochemical Properties and the Problem of Stability

A common property, characteristic of virtually all covalent organic perchlorates is a high risk of their explosion. The first investigators,[2,23] who obtained the simplest alkyl perchlorates, already noted that these highly volatile liquids (the boiling points of ethyl and methyl perchlorates are respectively 52° and 89 °C [23]) are very dangerous to handle. The perchlorates of monohydric alcohols[1,49] and also the lowest β-nitroalkyl[35] and β-nitratoalkyl[37] perchlorates are even more dangerous—these compounds are explosive even in solutions!

Furthermore, a very low thermal stability has been noted for many organic perchlorates: even at room temperature, these compounds char rapidly or polymerise. The low stability of covalent perchlorates is apparently due to the highly nucleofugitive nature of the perchloryloxy-group, i.e. the ease with which it can be expelled from the carbon skeleton with formation of carbonium ion intermediates (XXXV) and elimination products:



(XXXV)

The subsequent interaction of these species with one another leads to polymeric products. Evidently, perchlorates containing substituents capable of stabilising the carbonium ion (XXXV) formed and hence facilitating the heterolytic dissociation of the $C-OClO_3$ bond, will be the least stable. Indeed, according to the available literature data, t-alkyl perchlorates,[51,62] allyl perchlorates,[71] and benzyl perchlorates[106,107] are the least stable; when an attempt is made to obtain them by treating the corresponding halogeno-derivative with silver perchlorate in nitromethane, the mixture chars or a polymeric deposit is formed (molecular weight about 1000 [106,107]).

On the other hand, the presence of electron-accepting substituents in the molecule hinders the heterolysis of the $C-OClO_3$ bond, which usually increases the stability of the perchlorates. Thus perfluoroalkyl perchlorates can be stored at room temperature for years,[12,86] decomposing only slowly on heating to 200 °C, and are hardly hydrolysed by water. Trifluoromethyl perchlorate decomposes slowly on heating above 100 °C only in the presence of a catalyst—caesium fluoride:[12,88]

$$CF_3OClO_3 \xrightarrow{CsF} COF_2 + FClO_3.$$

The polyperchlorates of polyhydric alcohols[1] and *gem*-diperchlorates[56] are apparently more stable on heating than alkyl perchlorates. 2,2-Diperchloryloxypropane (I), obtained by Baum,[56] can be distilled without decomposition and explodes only on heating to 250 °C; however, *gem*-diperchlorates are exceptionally sensitive to the action of water.

Arenesulphonylmethyl perchlorates (XXXIV) have a high thermal stability.[11,104] These compounds melt without decomposition at temperatures above 100 °C but are extremely explosive.[11] It has been reported[108] that explosions of the single crystals in the diffractometer were observed during the X-ray diffraction analysis of toluene-*p*-sulphonylmethyl perchlorate.

It is interesting to note for comparison that covalent silyl perchlorates exhibit a higher stability than alkyl perchlorates.[18,72,73,109,110] Trialkylsilyl perchlorates $R_3SiOClO_3$ (R = CH_3, C_2H_5, n-C_3H_7, or t-C_4H_9) are oily liquids which fume in air and can be purified by vacuum distillation. The reaction of t-butyl dimethylsilyl perchlorates with alcohols can be used to introduce the trialkylsilyl protecting group.[18,110]

Skeletal perchlorates with a rigid carbon skeleton are more stable than alkyl perchlorates. The stable skeletal perchlorates (XIII), in which the perchlorate group is attached to a tertiary carbon atom, has been obtained.[16,17] Skeletal covalent secondary perchlorates, obtained by the present authors,[15] melt without decomposition at 120–150 °C, are insensitive to impact, and can be stored at room temperature for a long time without appreciable decomposition.

2. Identification

The problem of the identification of perchloric acid ester arose in the first studies on the synthesis of these compounds.[23,24,58] The highly explosive nature of covalent perchlorates precluded elemental analysis by combusting the specimen and hindered the use of chemical identification methods. The explosive decomposition of the lower perchlorates on heating in a capillary was used as a qualitative test for perchlorates.[68] The first quantitative methods for the determination of perchloric acid esters consisted in treating the specimen with an alcoholic solution of KOH with subsequent gravimetric determination of the precipitate of potassium perchlorate, which is insoluble in ethanol.[25] A more modern modification of this method consists in the titrimetric determination of the amount of alkali needed for the complete hydrolysis of the perchloric acid ester.[19,49] It has been found[62,69,71,102,103,111] that covalent perchlorates readily alkylate anisole and toluene in the *para*-position. In its analytical version, this reaction can also be used for the identification of perchlorates. The hydrolysis to alcohols with a known structure has likewise been employed to identify certain perchloric acid esters.[96]

New possibilities for the qualitative and quantitative determination of covalent perchlorates appeared after the development of spectroscopic techniques. The IR spectra of individual alkyl perchlorates were first obtained by Radell et al.[67] and intense absorption bands at 1230 and 1260 cm,$^{-1}$ [$\nu_{as}(ClO_3)$], in the range 1000 to 1100 cm^{-1} [$\nu_s(ClO_3)$], and near 700 cm^{-1} [$\nu(Cl-O)$], characteristic of covalent organic perchlorates, were found. There are no absorption bands in the range 1200–1300 cm^{-1} in the spectra of inorganic perchlorates. Subsequently, it was shown for a large number of perchlorates that intense bands in the range 1200–1300 cm^{-1} are present in the spectra of covalent organic perchlorates of any structure with different substituents[11,13,51] and can be used for the identification of these compounds.

Exceptional possibilities for the identification of perchloric acid esters are provided by NMR.[11,13,50,51,55,104] The presence of an electron-accepting substituent in the molecule (the perchloryloxy-group) results in a pronounced downfield shift of the signal. Thus the chemical shift of the α-proton attached to the perchloryloxy-group (solution in carbon tetrachloride) is 4.2 p.p.m. for methyl perchlorate and from 4.4 to 4.6 p.p.m. for n-alkyl perchlorates.[51] In the presence of a second electron-accepting substituent, the signal of the α-proton at the perchloryloxy-group shifts downfield even further; for example, it is 5.17 p.p.m. for 1-chloro-2-propyl perchlorate,[55] 5.56 p.p.m. for 2-fluoro-2,2-dinitroethyl perchlorate,[51] 6.3 p.p.m. for methylene diperchlorate, and 5.1–5.4 p.p.m. for arenesulphonylmethyl perchlorates.[11] ^{1}H NMR is very convenient for the determination of the yields of perchlorates without isolation from solution by integrating the spectrum of the specimen using a quantitative internal standard.[50,51,54,55,87,101-103]

Mass-spectrometric studies have been carried out only for perfluoroalkyl perchlorates[12,13,88,95] and β-bromoethyl perchlorate.[35] Molecular peaks have been detected in the mass spectra of trifluoromethyl perchlorate[12] and β-bromoethyl perchlorate.[35] Mass spectrometric data for the decomposition of perfluoroalkyl perchlorates with formation of the ClO_3^+, ClO_2^+, and ClO^+ fragments, but not ClO_4^+, have been used[12] to confirm their covalent structure.

Thin-layer[14,15,50,74] and gas–liquid[51,54] chromatographic methods have been employed for the identification and purification of covalent perchlorates. The thin-layer chromatography has proved very useful for the qualitative detection of covalent perchlorates: a characteristic property of these compounds is decomposition with formation of a black spot on moderate heating (100–150 °C) of the plate.[15,35]

Elemental analysis by combustion of the specimen has proved possible for the stable sulphonylmethyl,[11] perhalogenoalkyl,[12] and certain other perchlorates.[14,15,51,55,56]

X-Ray diffraction analysis has been used in recent years to establish the structures of a series of covalent perchlorates.[16,108,113-116] As a result of these investigations, the structures of toluene-*p*-sulphonylmethyl perchlorate[108] the skeletal perchlorate (XIII) of the trisecododecahedrane series,[16] as well as a series of skeletal secondary perchlorates having the tetracyclo[6.1.1.0^{2,7}0^{5,10}]-decane (XXXI) [113,114] and tetracyclo[5.3.0.0^{2,5}0^{3,8}]decane (XXXI) [115,116] carbon skeletons have been determined unambiguously.

3. Chemical Properties of Covalent Perchlorates

(a) General characteristics of the reactivity of covalent perchlorates. In the first studies on perchloric acid esters, it was already observed that these compounds are extremely reactive and enter especially readily into nucleophilic substitution reactions with water[23,96] and alcohols:[24]

$$\text{Alk}\,OClO_3 + ROH \rightarrow \text{Alk}\,OR + HClO_4,$$
$$R = H,\ \text{Alk}.$$

It was shown later that alkyl perchlorates exhibit a strong alkylating activity in relation to aromatic compounds.[65,111,112]

The high reactivity of covalent perchlorates, manifested even in reactions with weak nucleophiles, is due primarily to the fact that the perchlorate anion is a very effective leaving group or, in other words, is highly nucleofugitive. The alkylating capacity of covalent perchlorates varies within very broad limits as a function of the nature of the substituents and the structure of the carbon skeleton. t-Alkylperchlorates[51,62] as well as perchlorates of the allyl[71] and benzyl[106,107] series showed the most striking alkylating activity. The reactions of these perchlorates with nucleophiles apparently proceed via an S_N1 mechanism. Alkyl perchlorates with normal and secondary structures are less reactive and a bimolecular mechanism of the nucleophilic substitution of the perchlorate group is more characteristic of them. The introduction into the molecule of electron-accepting substituents such as a halogen[95,117] and the sulphonyl[10] or carboxy-groups[118] reduces the reactivity of the covalent perchlorate sharply: the abstraction of the ClO_4 group from the carbon atom in these perchlorates is very difficult and processes involving the dissociation of the $O-ClO_3$ bond become preferable.[10,117,118] Certain skeletal perchlorates [for example, compounds (XXXI) and (XXXII)], whose structural features hinder the attack by the nucleophile on the reaction centre, also exhibit a reduced reactivity.[118,119]

The reactions of covalent perchlorates have been studied in greatest detail in relation to methyl perchlorate[19-22,120-128] for a number of reasons. Firstly, methyl perchlorate is capable of undergoing nucleophilic substitution reactions even with very weakly nucleophilic species,[19,78,119,120,129,130] which permits the use of this compound as the substrate for kinetic studies designed to determine the nucleophilicity parameters in S_N2 processes.[121-124] Secondly, the markedly nucleofugitive properties of the perchlorate anion lead to certain anomalies in the kinetics of processes involving the nucleophilic substitution of the perchlorate group, which were initially actually interpreted as evidence in suport of a unimolecular reaction mechanism[123,124] and subsequently stimulated discussion[21,22,64,125] and a more profound study of these processes.[22] Finally, the perchlorate anion has solvation characteristics anomalous for an effective leaving group[126] and this leads to certain characteristic features of the kinetics of the hydrolysis of methyl perchlorate which are of theoretical interest.[19,126]

(b) Solvolysis of covalent perchlorates. Covalent perchlorates frequently enter into nucleophilic substitution reactions even with weakly nucleophilic species such as water and alcohol molecules. The highly nucleofugitive nature of the perchlorate anion leads to certain characteristics of the mechanisms of these processes. The problem of the solvolysis of covalent perchlorates attracted much attention after the publication of the studies[121-124] in 1967–1969 in which it was concluded, from a comparison of the activation entropies for the reactions of methyl perchlorate with certain nucleophiles, that the hydrolysis of this compound has an S_N1 mechanism in contrast to the S_N2 mechanism of methanolysis. This conclusion encountered sharp criticism[21,22,64,131] and gave rise to a number of kinetic studies devoted to a deeper understanding of the mechanism of the solvolysis of methyl perchlorate.[20-22,130,132] The rates of hydrolysis of methyl and ethyl perchlorates have been compared to determine the molecularity of the hydrolysis of methyl perchlorate.[64] In the case of a unimolecular mechanism, one would expect an appreciable acceleration of the hydrolysis after the introduction of the methyl group into the molecule, while for an S_N2 mechanism significant changes in rate in any direction can be usually observed. It was found[64] that the ratio of the rate constants for the hydrolysis of methyl and ethyl perchlorates is 0.8, which is within the limits established for a bimolecular mechanism in relation to a wide variety of leaving groups.

An alternative explanation of the kinetic features of the hydrolysis of methyl perchlorate in terms of Sneen's S_N2C^+ ion-pair mechanism.[133] However, this interpretation appears extremely unconvincing and has been justifiably rejected.[22,130,134] Kinetic data and especially data on the secondary isotope effect, which is observed in the hydrolysis of methyl perchlorate, have been explained within the framework of the traditional S_N2 mechanism and the hypothesis that the transition state in this reaction is looser than usual.[22] A more profound study of the nature of the transition state in the solvolysis of methyl perchlorate has been carried out using isotope effect data.[127] The values of the m constant in the Grunwald–Winstein equation, characterising the nature of the substrate, were used as evidence for the traditional S_N2 mechanism of the hydrolysis.[20,130] For the hydrolysis of methyl perchlorates in the methanol–water system, $m = 0.11$, which is characteristic of a typical S_N2 reaction. On the other hand, in the case of the S_N1 or the S_N2C^+ ion-pair mechanism one would expect $m = 1$.[130] In careful investigation of the kinetics of the solvolysis of covalent perchlorates in solvent systems with different ionising powers Y, a maximum was observed on the plots of the solvolysis rate constant against Y.[20,130] The presence of a region in which the rate of hydrolysis diminishses with increase in the concentration of water in the aprotic solvent (acetone or dioxan) was explained[20,130] by the unusual solvation characteristics of the perchlorate ion, which is more effectively solvated in a dipolar aprotic solvent than in water.[134]

The substitution of a hydrogen atom in methyl perchlorate by an electron-accepting group, such as the sulphonyl[10] and trifluoromethyl[171] groups, leads to other pathways in the solvolytic processes. In such cases, the oxidation-reduction decomposition with elimination of the chlorate anion becomes preferable.

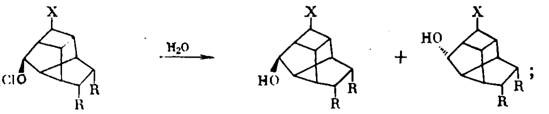
The mechanism of the solvolysis of arenesulphonylmethyl perchlorates has been studied in greatest detail.[11,135-141] The rate of solvolysis of these compounds is determined by the slow stage involving the deprotonation of the methylene group; the carbanion formed decomposes rapidly with formation of the chlorate anion, formic acid (or alkyl formate if the reaction is carried out in alcohol), and arenesulphonic acid.[135-141]

$$\begin{array}{l} ArSO_2CH_2OClO_3 + ROH \rightarrow ArSO_2\bar{C}HOClO_3 + R\overset{+}{O}H_2 \\ \qquad\qquad\qquad\qquad\qquad\qquad \downarrow ROH \\ \qquad\qquad\qquad\qquad\qquad ArSO_2H + HCOOR + ClO_3^- ; \end{array}$$

$Ar = p\text{-}NO_2C_6H_4, p\text{-}CH_3C_6H_4$; $R = H, CH_3, C_2H_5, t\text{-}C_4H_9, n\text{-}C_5H_{11}, CF_3CH_2$.

This pathway is apparently associated with the increased acidity of the methylene protons in arenesulphonylmethyl perchlorates as a consequence of the presence of two strong electron-accepting substituents in the molecule.

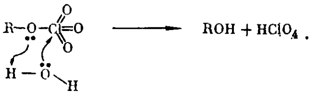
The pathway followed in the solvolysis of secondary perchlorates has been investigated solely in relation to skeletal perchlorates of the type (XXXI) and (XXXII), obtained by reactions involving the coupled electrophilic addition of the perchlorate group to olefins by the authors of the present review.[118] We investigated the reactions of covalent skeletal secondary perchlorates with water and $H_2{}^{18}O$ in acetone and dimethyl sulphoxide (DMSO) under various conditions. In all cases, the stereoisomeric hydroxy-derivatives (XXXVI) and (XXXVII) were isolated as the reaction products, the reaction in acetone proceeding preferentially with retention of configuration of the reaction centre and in DMSO with its inversion:



(XXXII) (XXXVI) (XXXVII)

X=Ar,I; R=CH_3,CO_2CH_3 .

The absence of selectivity in the hydrolysis and the results obtained for the distribution of the ^{18}O label can be explained[118] with the aid of a mechanism involving the attack by a water molecule on the chlorine atom in the perchlorate group:



Examples of such reactions in the series of inorganic perchloric acid derivatives are known,[51,53,54] but for covalent organic perchlorates the occurrence of processes determined by the attack on the chlorine atom by the nucleophile were not observed previously.

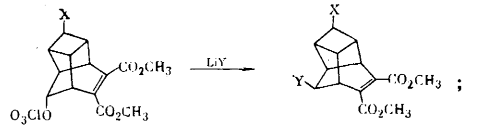
(c) Nucleophilic substitution reactions. Processes involving nucleophilic substitution in covalent perchlorates are of both theoretical[19,78,120,121,123,124] and practical[4,76,77] interest due to the high reactivity of these compounds. The kinetics of the reactions of methyl perchlorate with more than 20 different nucleophiles have been studied[123,124] in water and methanol in order to test the applicability of the Swain – Scott equation.[25] It was noted[123,124] that the rates of reaction of methyl perchlorate depend relatively slightly on the nature of the nucleophile, which is consistent with the idea that the perchlorate anion is a very effective leaving group. On the whole, it is concluded that these reactions have an S_N2 mechanism and that it is impossible to construct a general series in terms of the strength of the nucleophiles from the processes investigated.

The study of the kinetics of the reactions of methyl perchlorate with amines in water and methanol led to the conclusion[121] that these reactions, carried out with 25 amines, have a bimolecular mechanism. However, in the case of ammonia and butylamine the author put forward the hypothesis that there may be competition between S_N2 and S_N1 mechanisms. This hypothesis is doubtful bearing in mind the results of the polemics on the hydrolysis of methyl perchlorate (see the previous Section).

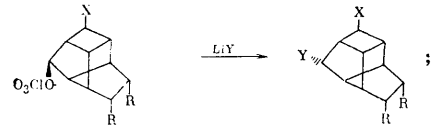
The kinetics of the reactions of a series of alkyl perchlorates (methyl, ethyl, isopropyl, and 2-adamantyl perchlorates) with *NN*-dimethylaniline in benzene have been studied recently.[19] On the basis of the kinetic parameters and especially the absence of an appreciable H/D isotope effect, it was shown that these reactions proceed via a classical S_N2 mechanism and that the second order rate constants decrease in the sequence Me > Et > iso-Pr $\gg$ 2-Ad.

The high reactivity of the covalent perchlorates is clearly manifested in relation to their reactions with weak nucleophiles such as arenesulphonate anions.[119,120] In a study of the kinetics of the reactions of various tetrabutylammonium arenesulphonates with methyl perchlorate in acetonitrile, the reaction was found to be of second order and it was established that the rate constants are independent of the concentration of the salt.[120] On the other hand, in the bimolecular reaction of silver toluene-*p*-sulphonate with methyl perchlorate, a decrease in the rate constant was observed with increase in the concentration of silver toluene-*p*-sulphonate, which is apparently a consequence of the decrease in the nucleophilicity of the anion as a result of the formation of close ion pairs with the silver cation.

The present authors investigated the stereochemistry of the reactions of skeletal covalent secondary perchlorates with a series of nucleophiles, including arenesulphonate anions (in relation to the toluene-*p*-sulphonate anion.[119] It was shown that the reactions of the perchlorates (XXXI) and (XXXII) with the nucleophiles proceed with complete inversion of the configuration at the reaction centre, which constitutes convincing evidence in support of the S_N2 mechanism:



(XXXI) , X=SAr; Y=Cl,Br .



(XXXII). X=SAr,I; R=CH_3,CO_2CH_3; Y=Cl,Br, p-NO_2–$C_6H_4SO_3^-$.

The reactions investigated can serve as a convenient method for introducing various substituents into the molecule of a skeletal compound.

Several studies in which covalent compounds were used for synthetic purposes as alkylating agents have been published in recent years.[76,77] For example, methyl perchlorate can be used to alkylate sugars[77] and certain heterocyclic compounds.[76] Unfortunately, the number of such studies is very limited, but further investigations in this field will undoubtedly lead to the discovery of new synthetic applications of the highly reactive covalent organic perchlorates.

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It is seen from the data examined in this review that covalent organic perchlorates have become a class of accessible compounds suitable for various chemical reactions. Although the possibilities for their practical application are held back by the potential and frequently real risk of explosion of perchloric acid esters, nevertheless in most cases this obstacle can be readily eliminated by employing them without intermediate isolation in the form of safe solutions in inert solvents. Furthermore, studies on the reactivity of covalent perchlorates have demonstrated that the perchlorate anion is one of the best leaving groups. The data obtained constitute a basis for the practical utilisation of covalent perchlorates in synthesis as reagents with a stronger alkylating activity than the traditional toluene-*p*-sulphonates and other organic sulphonates. Another distinctive feature is that substitution in perchloric acid esters takes place via an S_N mechanism. Thus a basis has been created for stereospecific syntheses, which also constitutes an advantage of alkyl perchlorates over traditional alkylating agents.

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