THERMAL STABILITY OF PERCHLORIC ACID

By

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Studies related to the homogeneous and heterogeneous thermal decomposition as well as to the high temperature reaction of perchloric acid are reviewed. A critical survey of the reaction mechanisms is given.

Introduction

In the last decade there has been considerable interest in the chemistry of perchloric acid mainly because it is the primary dissociation product of ammonium perchlorate, the most widely used solid oxidizer. It has been assumed that perchloric acid and/or its reactive decomposition products play a predominant role in the oxidation processes of ammonium perchlorate. The study of the reactions of perchloric acid and the elucidation of their kinetics and mechanism therefore provides very valuable information for the evaluation of the decomposition mechanism of ammonium perchlorate. The aim of the present paper is to summarize the considerable experimental material obtained in this field with emphasis on the more important results and conclusions.

Liquid phase decomposition of $HClO_4$

Very varied opinions have been expressed on the thermal stability of perchloric acid in the early literature. Recent investigations have not confirmed the high instability of even anhydrous perchloric acid and its explosibility was attributed to the presence of Cl_2O_7.

The thermal decomposition of perchloric acid was studied first in the liquid phase. ZINOVJEV *et al.* studied the reaction by measuring the volume of oxygen evolved [1]. The decomposition can be described by the following reaction equation

$$HClO_4 = 1/2\,Cl_2 + 1/2\,H_2O + 7/4\,O_2. \qquad (1)$$

The reaction

$$HClO_4 = HCl + 2\,O_2 \qquad (2)$$

does not play any important role. They could detect a small amount of chlorine oxides as intermediates. The decomposition curve consisted of three stages:

(*i*) time lag, where no detectable decomposition occurs,
(*ii*) acceleration period,
(*iii*) decay period.

From the temperature dependence of the maximum rate of oxygen evolution, 22.2 kcal/mole activation energy was obtained. Some decomposition curves of the perchloric acid in liquid phase are shown in Fig. 1.

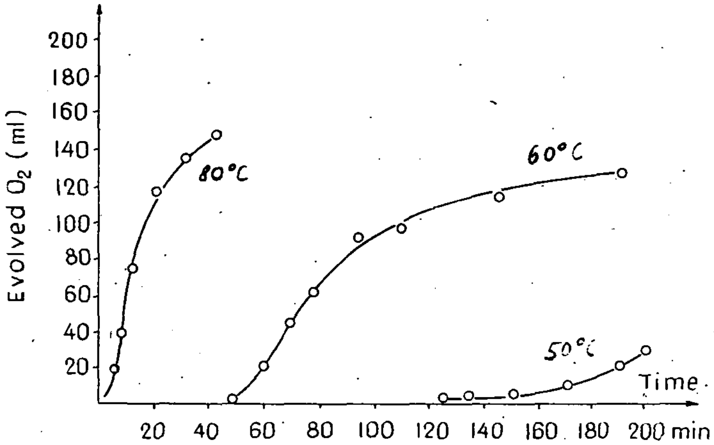


Fig. 1. Thermal decomposition of liquid perchloric acid at various temperatures [1].

In a study by TSENTSIPER [2] activation energy of 22.5 kcal/mole was calculated. The dilution of $HClO_4$ influenced the rate of decomposition; this observation served as one of the clues in evaluating the mechanism of decomposition. This phenomenon was attributed to a decrease in the concentration of the covalent form of $HOClO_3$ and to an increase in the concentration of the acid form, ClO_4^-, which is more stable than the previous one. The first step of decomposition is the rupture of the HO—ClO_3 bond, which is followed by a chain reaction.

The analysis of the dependence of the induction periods upon the temperature yielded a value of 32.6 kcal/mole [3]. The induction period increased with the acid concentration. The activation energy of the decomposition, however, was independent of the concentration of the acid in the range between 84.8 and 100%. In a similar way, an activation energy of 32.5 kcal/mole was obtained for the decomposition of $HClO_4 + Cl_2O_7$ mixtures. For the acceleration period an activation energy of 22.5 kcal/mole was calculated.

These values approached quite closely the value obtained for the decomposition of Cl_2O_7 in the gas phase. An interesting result of this work was that the addition of inhibitors, such as trichloroacetic acid and carbon tetrachloride, reduced the rate of decomposition. A similar observation was recorded by MISSAN and SUKHOTIN [4] in the presence of chloral hydrate.

Based on the above observations and on the fact that the activation energies of the decomposition of anhydrous perchloric acid and Cl_2O_7 in the gas and in the liquid phases are practically the same, ZINOVJEV [3] has assumed that the rate of decomposition of perchloric acid is determined by the formation and subsequent decomposition of Cl_2O_7

$$2\,HClO_4 \rightleftharpoons Cl_2O_7 + H_2O \tag{3}$$

The reaction is promoted by the tendency of perchloric acid to form a hydrate. This suggestion, however, is not supported by the decomposition characteristics of Cl_2O_7 which are basically different from those of the anhydrous acid [5, 6].

Gas phase decomposition of $HClO_4$

The first detailed kinetic investigation on the thermal decomposition of perchloric acid in gas phase was carried out by LEVY [7]. His results showed that perchloric acid is stable below 200 °C. A slow decomposition in the static system was observed at 200 °C. The reaction was followed by measuring the rate of chlorine formation colorimetrically. In the temperature range 210 and 400 °C the equation

$$HClO_4 = 0.5\,H_2O + 0.5\,Cl_2 + 1.75\,O_2 \tag{4}$$

represents the sole stoichiometry of the decomposition. Between 200 and 350 °C the reaction was found to be first order. The Arrhenius plot of the data shows two lines of different slopes (Fig. 2); one between 200 and 315 °C and another between 315 and 400 °C. The slope in the low temperature range corresponds to 10 kcal/mole activation energy while the slope in the high temperature range and the rate

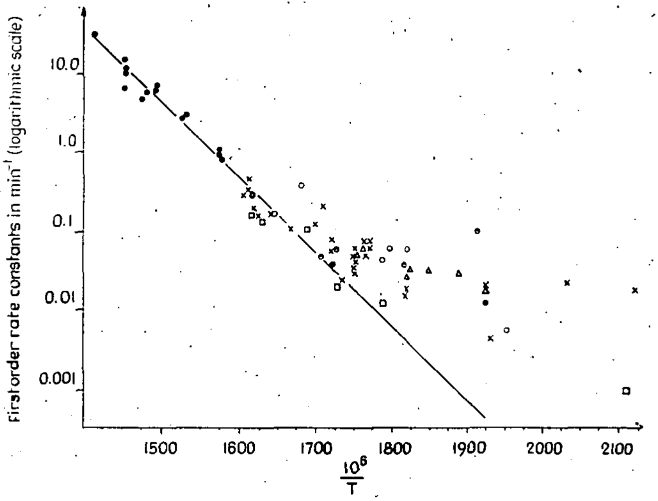


Fig. 2. Arrhenius diagram of the decomposition of perchloric acid vapour [7].

× Runs without special washing
○ Pre-rinsed runs
□ Runs in quartz
△ Runs with inert gas
◒ Packed runs
● Flow system runs

constants of flow rate measurements yielded 45.1 kcal/mole activation energy. On investigating the effect of the surface and its treatment it was concluded that the surface of the reaction vessel was very important between 200 and 310 °C, but its influence was unsignificant above this temperature. Small amounts of water exhibited a moderate inhibiting effect without influencing the kinetics significantly.

LEVY postulated the following mechanism for the decomposition of perchloric acid. The primary step of decomposition was assumed to be

$$HOClO_3 = HO + ClO_3 \tag{5}$$

followed by the fast steps

$$HO + HOClO_3 = H_2O + ClO_4 \tag{6}$$

$$ClO_4 = 0.5\,Cl_2 + O_2 \tag{7}$$

$$ClO_3 = 0.5\,Cl_2 + 1.5\,O_2 \tag{8}$$

For the heat of reaction of the first step 40.3 kcal/mole was obtained using the heats of formation of $HOClO_3(g)$ − 2.3 kcal/mole, $HO(g)$ 8.96 kcal/mole and of $ClO_3(g)$ 37 kcal/mole. This is somewhat higher than the measured activation energy.

The thermal decomposition of anhydrous perchloric acid in the gas phase has been studied by SIBBETT *et al.* and DIETZ [8—10]. Unfortunately the results of SIBBETT were published in special reports which had only a restricted distribution. Some details can be found, however, about this investigation in a review by PEARSON [11].

SIBBETT and LOBATO [8] found that decomposition takes place in the direction of chlorine formation. The reaction at 200 °C was found to be of the second order up to 70—80% decomposition and then of the first order up to 95% decomposition. With the increase of the reaction temperature the predominance of second order kinetics decreased. They observed that both the first and second order rate constants increased as the surface to volume ratio increased. In an extensive study at temperatures between 150 and 260 °C the amount of evolved chlorine was found to be proportional to the quantity of decomposed acid.

Computer calculation showed that the reaction scheme best fitting the data is

$$2\,HClO_4 \xrightarrow{k_1} H_2O + Cl_2 + 7/2\,O_2 \tag{9}$$

$$HClO_4 + H_2O \rightarrow HClO_4 . H_2O \tag{10}$$

$$HClO_4 . H_2O \xrightarrow{k_2} 1/2\,Cl_2 + 3/2\,H_2O + 7/4\,O_2 . \tag{11}$$

Assuming that these reactions occur on the reactor surface the following rate equation was obtained

$$\frac{-d[HClO_4]}{dt} = 2\,k_1[HClO_4]^2 + \frac{k_2[HClO_4][H_2O]}{1 + K_B[H_2O]} \tag{12}$$

where K_B is the equilibrium constant for the adsorption of some inhibiting species (probably water) on the surface.

Further consideration suggested that the reaction proceeds according to a mechanism in which perchloric acid is weakly adsorbed and the surface covered only slightly. The rate equation for the initial bimolecular process is

$$V_1 = 2\,k_1'k^2[HClO_4]^2, \tag{13}$$

where k_1 is the experimental rate constant which is equal to $k_1'K^2$, and K is the equilibrium constant for the adsorption of perchloric acid on glass. The activation energy of the decomposition can be expressed as

$$E_{a_1} = E_T - 2\,\lambda_{HClO_4} \tag{14}$$

where E_T is the true activation energy of decomposition of perchloric acid in the homogeneous vapour phase and λ_{HClO_4}. is the heat of adsorption of perchloric acid.

Two species, namely perchloric acid and water (as the inhibiting reaction product), were considered in the adsorption process. If they compete for the same sites, the correlation

$$E_{a_2} = E_T - \lambda_{H_2O} \tag{15}$$

is valid, but if they are adsorbed on two different sites of the surface, *i.e.* in the case of competitive adsorption, the equation,

$$E_{a_2} = E_T - \lambda_{H_2O} - \lambda_{HClO_4} \tag{16}$$

becomes dominant. For E_{a_1} and E_{a_2} the experimentally determined values were 13.4 and 20.5 kcal/mole. For the heat of adsorption of water on pyrex glass the value is 13.3 kcal/mole. When SIBBETT *et al.* made this calculation, only the activation energy for liquid phase decomposition, 32.8 kcal/mole, was available. Using this value for E_T they obtained 9.7 kcal/mole for the heat of adsorption of perchloric acid. By substitution of this value along with the others in equations (15, 16) they obtained 33.8 and 43.4 kcal/mole, respectively. They concluded that the competitive adsorption was more probable.

Recalculation of these values, however, with the activation energy of the homogeneous decomposition of perchloric acid in the gaseous phase (45.1 kcal/mole) resulted in 33.8 and 49.65 kcal/mole, from which PEARSON [11] concluded that the non-competitive adsorption process is the more probable one.

A recent work of GILBERT and JACOBS [12] studying the effects of different pretreatments of the Pyrex glass reaction vessel has thrown more light on the heterogeneous nature and on the mechanism of the decomposition of perchloric acid.

Pretreatment of the reaction vessel involved:

a) annealing,

b) washing with a mixture of concentrated sulphuric acid and potassium permanganate, followed by washing with a mixture of nitric acid and hydrogen peroxide,

c) coating with boric acid.

In agreement with the previous workers, GILBERT and JACOBS found that the reaction is essentially of the first order in the temperature range studied, *i.e.* between 279 and 471 °C in annealed, aged and washed reaction vessels. A slightly autocatalytic decomposition was found, however, in the washed vessel. A significant deviation from first order kinetics was observed at high conversions in the intermediate temperature range.

The rate constants obtained using the annealed reaction vessel lie on a curve, while those for the washed vessel correspond more closely to a straight line (Fig. 3). At high temperatures the curve approaches this line. In their interpretation of this phenomenon the authors assumed that there are two parallel reactions, a homogeneous one which predominates at high temperatures and a heterogeneous one which predominates at low temperatures.

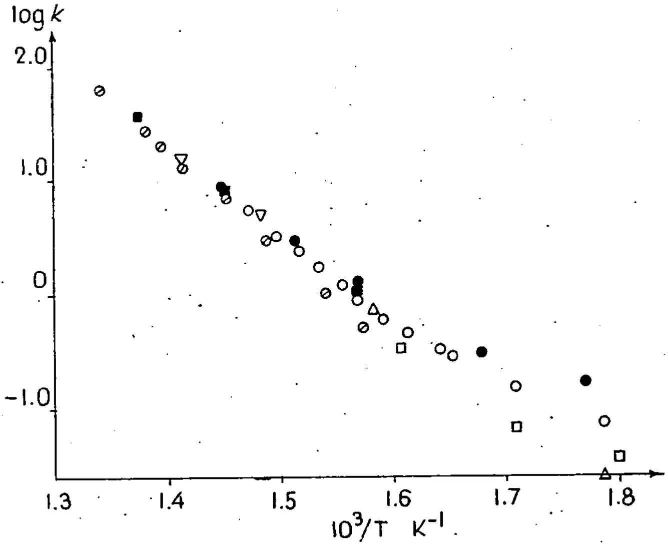


Fig. 3. Arrhenius diagram of the first order rate constants of the thermal decomposition of perchloric acid [12]. ○ annealed reaction vessel I; □ annealed reaction vessel I, aged; △ aged reaction vessel I, packed; ▽ washed reaction vessel I; ⊘ washed reaction vessel II; ■ reaction vessel IV, annealed. The rate constant k is given in $\min^{-1}$.

In the reactors which have not been annealed the heterogeneous reaction is the predominant one up to the highest temperatures. The specific rate constant for the heterogeneous reaction on freshly annealed pyrex glass is given by

$$k = 125 \exp[-16.000/RT] s^{-1} cm^{-2}. \tag{17}$$

It has been assumed that the homogeneous reaction in the gas phase is a simple unimolecular reaction and the proposed mechanism is essentially the same as has been put forward by LEVY. For the low temperature heterogeneous decomposition various models have been considered:

(*i*) Heterogeneous decomposition is of the first order on Pyrex glass. This model fails to explain both the deviations from first order kinetics at high conversion and the unfavourable effect of packing the reactor with glass wool.

(*ii*) As a possible reason the heterogeneous removal of the hydroxyl radical was suggested, assuming that the OH radicals are responsible for half of the decomposition of perchloric acid and that the bimolecular heterogeneous removal of OH radicals is competitive.

The rate equation derived for the steady state is

$$\frac{-\mathrm{d}[\mathrm{HClO_4}]}{\mathrm{dt}} = [\mathrm{k_1}+\mathrm{k_1'}][\mathrm{HClO_4}]+\frac{\mathrm{k_2^2}[\mathrm{HClO_4}]^2}{\mathrm{k_3}} \qquad (18)$$

k_1 = rate constant of reaction (5)
k_1' = rate constant of the heterogeneous reaction (5)
k_2 = rate constant of reaction (6)
k_3 = rate constant of the bimolecular reaction of OH radicals.

A certain difficulty was caused by the fact that increasing the rate of the latter process increase of the surface area would result in a reduced decomposition rate. Nevertheless, this model was dismissed, since the above process would play an important role if the reaction had to a significant degree a second order character; but this is so only at very high partial pressures of perchloric acid.

(*iii*) The mechanism of the decomposition of perchloric acid containing the least unexplained features involves a chain reaction and termination steps.

In spite of its non-reactivity the ClO radical was assumed as a possible chain carrier. It might be formed in the reaction

$$\mathrm{HClO_4} = \mathrm{ClO}+\mathrm{O_2}+\mathrm{OH} \qquad (19)$$

and in the corresponding heterogeneous reaction. The further steps are the following:

$$\mathrm{ClO}+\mathrm{HClO_4} \overset{\mathrm{k_2}}{=} \mathrm{ClOH}+\mathrm{O_2}+\mathrm{ClO_2} \quad -18.9\ \mathrm{kcal} \qquad (20)$$

$$\mathrm{ClOH}+\mathrm{HClO_4} \overset{\mathrm{k_3}}{=} 2\,\mathrm{ClO}+\mathrm{H_2O}+\mathrm{O_2} \quad +14.9\ \mathrm{kcal} \qquad (21)$$

$$2\,\mathrm{ClO} \overset{\mathrm{k_4}}{=} \mathrm{Cl_2}+\mathrm{O_2}. \quad -48.4\ \mathrm{kcal} \qquad (22)$$

This model explains the observed departures from the first order behaviour only if the ClO radicals — in addition to the homogeneous termination step (22) — are removed heterogeneously by the reaction

$$\mathrm{ClO} \overset{k_5}{=} \frac{1}{2}\mathrm{Cl_2}+\frac{1}{2}\mathrm{O_2}. \qquad (23)$$

The following simplified rate equation was derived:

$$-\frac{d[\mathrm{HClO_4}]}{\mathrm{dt}} = \left[\mathrm{k'}-\frac{\mathrm{k_2k_5}}{\mathrm{k_4}}\right][\mathrm{HClO_4}]+\frac{\mathrm{k_2^2}}{\mathrm{k_4}}[\mathrm{HClO_4}]^2 \qquad (24)$$

where

$$\mathrm{k'} = \mathrm{k_1}+\mathrm{k_1'}$$

In this case, increase of the surface area increases both k_1' and k_5; thus the overall rate may either increase or decrease, depending upon the relative effects. Kinetic data for the decomposition of $HClO_4$ are collected in Table I.

Table I

Kinetic data of the homogeneous decomposition of perchloric acid

State	Concentration, %	Temp. range, °C	Activation energy kcal/mole	Kinetic equation	Frequency factor, s^{-1}	References
Liquid			22.2	W_{max}		[1]
			22.5	W_{max}		[2]
	85.5 – 100		32.6	τ_0		[2]
	$HClO_4 + {} + Cl_2O_7$		32.5	τ_0		[2]
			22.5	rate of acceleration period		[2]
Gas	72.4	200—310	10.0	first order (HT)		[7]
	72.4	315—400	45.1	first order (HM)	$5.8 \cdot 10^{13}$	[7]
	72.4	279—350	16.0	first order (HT)	$2.0 \cdot 10^{13}$	[12]
	72.4	355—471	43.0	first order (HM)	$6.7 \cdot 10^{12}$	[12]
	100	150—260	8.9	second order (HT)		[9]
	100	150 – 260	21.3	first order (HT)		[9]

W_m = rate maximum; HT = heterogeneous decomposition on the wall; τ_0 = induction period; HM = homogeneous decomposition.

Mass spectrometric studies

The thermal decomposition of perchloric acid has been studied also by mass spectrometry [13]. At about 1000 °C the reaction is mainly heterogeneous and the predominant mode of decomposition is

$$HOClO_3 = HCl + O_2. \tag{25}$$

The presence of HCl was explained in terms of the following equilibrium

$$2\,HCl + 1/2\,O_2 \longrightarrow Cl_2 + H_2O. \tag{26}$$

No intermediates were found.

The mass-spectrometric investigations of FISCHER [14] on the thermal decomposition of perchloric acid resulted in a different picture. On admission of constant boiling (72 wt. %) perchloric acid into the mass spectrometer there was an initial conditioning period of several hours during which the predominant peaks were those of HCl and O_2. These peaks gradually decreased to be replaced by the reproducible mass spectrum. This is shown in Table II.

Table II

Electron impact mass spectra of perchloric acid (72%) [13, 14]

m/e	Species	% of the ClO_2^+ peak	% of the $HClO_4^+$ peak
28	N_2, CO	0.045	
32	O_2	0.09	1.57
35	^{35}Cl	0.09	6.08
36	$H^{35}Cl$	0.1	25.6
37	^{37}Cl	0.029	1.86
38	$H^{37}Cl$	0.038	8.51
44	CO_2	0.083	—
51	^{35}ClO	0.281	3.09
52	$H^{35}ClO$	0.024	2.18—6.17
53	^{37}ClO	0.097	1.21
54	$H^{37}ClO$	0.007	0.88—2.08
67	$^{35}ClO_2$	0.69	4.66
68	$H^{35}ClO_2$	0.024	0.39—0.94
69	$^{37}ClO_2$	0.236	2.05
70	$H^{37}ClO_2$	0.014	0.57
74	$^{37}Cl_2$		0.11
83	$^{35}ClO_3$	1.00	2.15
84	$H^{35}ClO_3$		0.28
85	$^{37}ClO_3$	0.34	0.95
86	$H^{37}ClO_3$		0.08
100	$H^{35}ClO_4$	0.646	1.00
102	$H^{37}ClO_4$	0.215	0.34

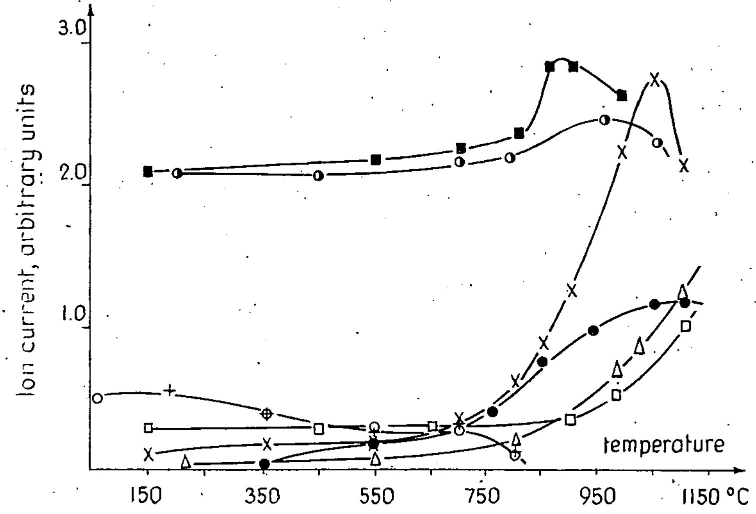


Fig. 4. Thermal decomposition of perchloric acid at various temperatures followed by electron impact mass spectrometry [14]. O, $HClO_4$; +, ClO_3; ●, O_2; △, Cl_2; □, HCl; X, ClO; ◐, HOCl. For clearer presentation the curves for ClO_2 and HOCl have been raised by 2 units.

Fig. 4 shows the change in ionic current as the function of temperature for different ions in the mass spectrum of perchloric acid. The curves were divided into three zones. The first, at about 800 °C, was ascribed to the decomposition of $HClO_4$ and to the decrease in $HOClO_3^+$ and ClO_3^+. The ClO_3^+ ion observed in the first phase of decomposition resulted presumably from the dissociative ionization reaction

$$HOClO_3 + e = ClO_3^+ + O + H + 2e. \tag{27}$$

The second zone, at about 950 °C, is associated with the pyrolysis of ClO_2, with the decrease of ClO_2^+, and the third, at about 1100 °C, with the decomposition of ClO.

There was no indication of a heterogeneous reaction, nor evidence of the reaction

$$HOClO_3 = HCl + 2\,O_2 \tag{28}$$

suggested by MAJER and HEATH [13].

No peaks corresponding to Cl_xO_y ($x > 1$), to the ClO_2 isomer Cl—O—O, or to the ClO_3 radicals were observed.

The proposed scheme for the decomposition of perchloric acid vapour is as follows:

$$HOClO_3 \rightarrow ClO_3 + OH \tag{29}$$

$$ClO_3 \rightarrow ClO_2 + O \tag{30}$$

$$ClO_3 \rightarrow ClO + O_2 \tag{31}$$

$$ClO_2 \rightarrow Cl + O_2 \quad 47\ \text{kcal} \tag{32}$$

$$ClO_2 \rightarrow ClO + O \quad -13\ \text{kcal} \tag{33}$$

$$ClO \rightarrow Cl + O \tag{34}$$

The radicals might dimerize (Cl, O) or react on the wall (Cl, ClO, OH) yielding HCl, ClOH, H_2O.

The main intermediate of decomposition is the ClO radical which arises primarily from the ClO_3 radical. ClO_2 was not considered as an important source of ClO radicals. It is assumed that ClO radicals are responsible for the enhanced reactivity of perchloric acid — fuel flames.

The data collected in Table II show that due to electron impact a significant fragmentation of perchloric acid occurs in the ionization chamber of the mass spectrometer. This fact causes a considerable difficulty when mass spectrometry is applied to the analysis of the reaction products of compounds containing perchloric acid, especially in the case of ammonium perchlorate decomposition. Unfortunately, the lowering of the electron beam energies yielded almost the same spectra. The method of field-ionization provided a solution to this problem.

In the case of field-ionization the molecules on the metal surface are ionized due to an extremely high electrostatic field ($> 10^7$ V/cm). The positive ions thus formed are immediately accelerated into the mass analyzer by an external field. Since there is only a small energy transfer from the impinging particles, field ions have little or no excess energy left to cause fragmentation. The relative parent molecular ion intensities of the unstable parent compounds are considerably enhanced compared to the 70 eV or low voltage electron impact ionization.

As a first attempt in this line, SOLYMOSI and BLOCK [16] investigated the field ionization of perchloric acid. The basic aim was to work out experimental conditions under which the field ionization of perchloric acid occurs with practically insignificant fragmentation.

Platinum and tungsten with a radius of curvature of 500 to 2000 Å were tested as field emitters. These were introduced into the field ion source connected to a tungsten loop for heating and temperature control. The field ion source was connected to a CH4 Atlas MAT mass-spectrometer.

The following factors were examined: (*i*) effect of the field; (*ii*) effect of the partial presure of perchloric acid; (*iii*) effect of water; (*iv*) effect of temperature.

Both Pt and W tips were stable enough for the field ionization of perchloric acid. After a certain conditioning period, the field ion current showed a remarkable stability and the Pt-tip had a life-time of more than 100 hours of operation. Some field ion mass spectra are shown in Table III. If the electron impact and field ion mass spectra are compared, it appears that the latter are significantly simpler with a much less pronounced fragmentation on both metal tips. In addition however, there are ions in the field ion mass spectra which never appear in electron impact spectra. These are $H.HClO_4^+$, $HClO_4.H_2O^+$, $HClO_4.2\,H_2O^+$, $HClO_4.H_3O^+$ and ClO_4^+ ions. The intensities of $HClO_4^+$, $HClO_4.H_2O^+$ and their ratios are shown as function of the applied field in Fig. 5.

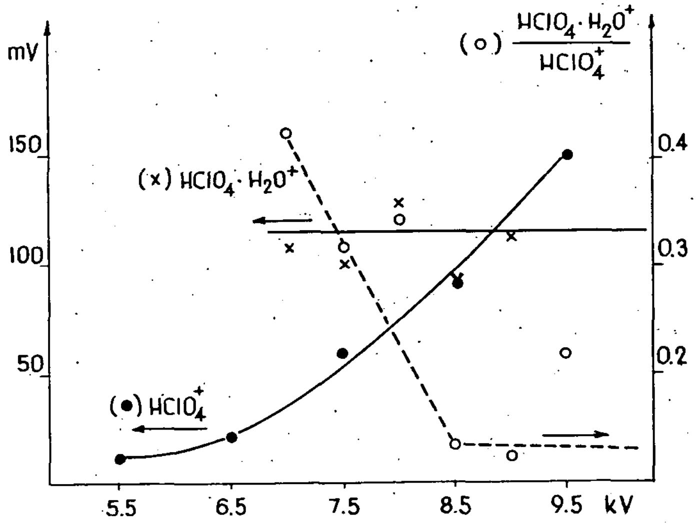


Fig. 5. Intensities of $HClO_4^+$, $HClO_4 \cdot H_2O^+$ and their ratios as functions of the applied field. Tungsten emitter, $T = 25$ °C, $p_{HClO_4} = 4 \cdot 10^{-6}$ torr [16]

The intensity of $HClO_4^+$ ions increased continuously with increasing field; the contribution of the hydrated perchloric acid ions, however, remained constant.

In the case of W the main fragment ions were the ClO_3^+ ions. The dependence of the absolute and relative intensities of ClO_3^+ ions upon the applied field is shown in Fig. 6.

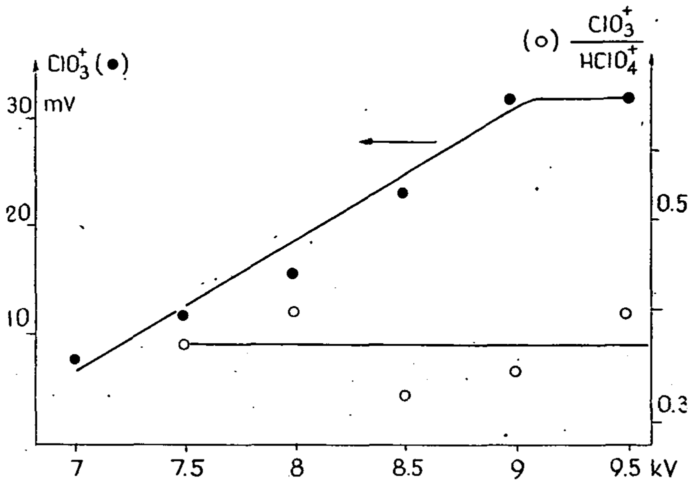


Fig. 6. Absolute and relative intensities of ClO_3^+. Tungsten emitter, $T = 25\ °C$, $p_{HClO_4} = 4 \cdot 10^{-5}$ torr [16].

Table III

Field ionization mass spectra of $HClO_4$ on W and Pt emitters, [16].

m/e	Species	as % of the $HClO_4$ peak W	Pt
32	O_2	—	3.7
35	^{35}Cl	—	—
36	$H^{35}Cl$	1.43	4.6
51	^{35}ClO	0.33	0.77
52	$H^{35}ClO$	0.44	4.00
55	$H_3O \cdot (H_2O)_2$	24.39	1.0
67	$^{35}ClO_2$	9.89	3.0
68	$H^{35}ClO_2$	2.96	—
70	Cl_2, $H^{37}ClO_2$	0.93	1.2
83	$^{35}ClO_3$	39.56	6.3
84	$H^{35}ClO_3$	—	—
99	$^{35}ClO_4$	2.63	0.46
100	$H^{35}ClO_4$	100	100.0
101	$H^+ \cdot H^{35}ClO_4$	—	2.9
118	$HClO_4 \cdot H_2O^+$	33.1 (7.5 kV)	—
136	$HClO_4 \cdot 2\ H_2O^+$	12.0 (7.5 kV)	—

Pressure of $HClO_4$ (72%) $= 4 \cdot 10^{-5}$ torr, u_0 (field) $= 9.5$ kV

It appears that the field ionization mass spectra of perchloric acid are significantly different on Pt and W tips resp. The basic differences are:

(*i*) The fragmentation of the $HClO_4^+$ ion is much greater on W tips than on Pt tips.

(*ii*) In the case of Pt emitter there was no convincing indication of the formation of either $HClO_4.H_2O^+$ or $HClO_4.2\,H_2O^+$ ions; on the W emitter these ions could be easily identified.
(*iii*) Only extremely small amounts of $H.HClO_4^+$ ions were formed on the W emitter.

From the comparison of the relative intensities of field ions two phenomena have emerged. First, the ionization probabilities of different neutral compounds at or near the surface are different. Thus, field ion intensities will not allow a quantitative comparison of neutral concentrations. If the ionization step is merely an electron tunneling into the emitter tip, ionization potentials may be a rough indication of the order of detectability: ClO_2 (10.7 eV); ClO (11.1 eV); ClO_3 (11.7 eV); $HClO_4$ (13.4 eV); O_2 (12.06 eV); H_2O (12.6 eV) Accordingly, the most interesting chlorine oxides may be easily detected and have a commensurable ionization probability which is somewhat higher than that of $HClO_4$ and water.

Secondly, the ionization at a field intensity of 10^7 to 10^8 V/cm may occur either with or without chemical surface interaction at a distance of several Å from the emitter surface. Since the emitter material has a specific influence, most of the observed processes will be induced by surface interaction at a high electric field. On the other hand, not all of the detected ions are related to these processes. The occurrence of metastable ions, as in the case of the reaction $HClO_4^+ \rightarrow ClO^+ \ldots$, is convincing evidence of a homogeneous decay process.

The $HClO_4^+$ and H_2O^+ ions are formed by tunneling of an electron into the emitter

$$HClO_4 \xrightarrow{\text{field}} HClO_4^+ + e^-_{(Me)} \tag{35}$$

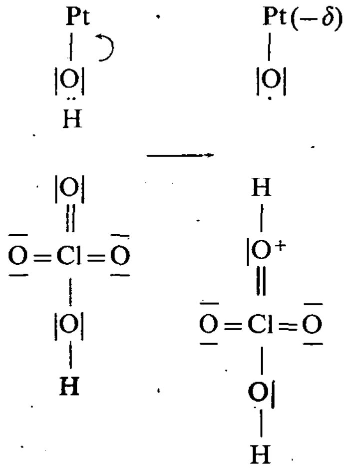
$$H_2O \xrightarrow{\text{field}} H_2O^+ + e^-_{(Me)}\,. \tag{36}$$

The process is promoted by intermolecular interactions, but not necessarily affected by some particular surface structure. Since the ionization potential of water is lower, its field ionization probability exceeds the ionization of perchloric acid.

The different behaviours of Pt and W tips were ascribed to their different chemical properties. The study of the field ionization of H_2O indicated a great difference between the two emitters and pointed to the great importance of the adsorption layer of water in the formation of different associates such as H_3O^+, $H_3O^+.H_2O$, $H_3O^+.(H_2O)_2$ and $H_3O^+.(H_2O)_3$. The probability of the formation of these ions depended sensitively on the field which influenced the adsorption layer.

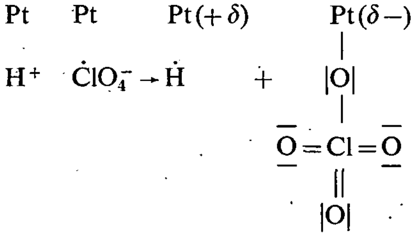
It was noticed that the surface of W tips is partially oxidized during the interaction with perchloric acid. This surface oxidation is very fast and occurs even at the very beginning of the interaction of perchloric acid and metal tip. As the field ion mass spectra show, the formed tungsten oxides evaporate at higher field and thus the W surface is regenerated and oxidized again. It was assumed that the affinity of the W emitter to water, and more likely, the affinity of partially oxidized W to water is much larger than that of the Pt surface. The fact that the ions of mono and dihydrate perchloric acid were formed only on W tip was attributed to the pronounced adsorption of water. The formation of ions of hydrated perchloric acid on W surface was described by interaction of $HClO_4$ with surface H_2O molecules without attached protons, by simple electron transfer. For this mechanism a heavily oxidized metal surface is required. The importance of the oxidized state of the W surface for the formation of ions of hydrated perchloric acid is indicated by the observation that on W tips which have been treated with $HClO_4$ at higher temperatures for still deeper oxidation, the intensities of $HClO_4.H_2O^+$ and $HClO_4.2\,H_2O^+$ increased and even exceeded that of $HClO_4^+$ at room temperature.

On the platinum surface water will be less strongly adsorbed and be ionized as H_2O^+, H_3O^+ or $H_3O^+\cdot(H_2O)_n$. The formation of the protonated monomer is probably due to surface hydroxyls:



(37)

or to a dissociatively adsorbed perchloric acid molecule



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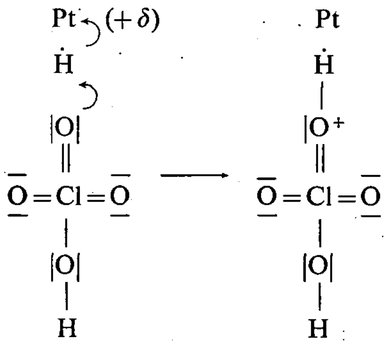


(39)

Both these mechanisms would explain the presence of $H \cdot HClO_4^+$ ions and the absence of hydrated molecules on Pt emitters.

A further question is the origin of the other ions beside the parent ions. It is to be noted that the product distribution of $HClO_4^+$ field ion fragmentation differed markedly from that of the heterogeneous catalytic decomposition of perchloric acid followed by field ion mass spectrometry. The formation of the fragment ions was tentatively explained by the decomposition of $HClO_4^+$ ion in the adsorption layer. There was only very little decomposition of $HClO_4^+$ ion on the way from the emitter to the detecting chamber. Actually a metastable ion indicating this kind of process was found only in one case.

Catalytic decomposition of perchloric acid vapour

The first direct evidence of the catalytic effect of oxides on the decomposition of perchloric acid was published in 1968 [17]. Chromium oxide was found to be the most active catalyst and its effect has later been studied in more detail [18]. Its excellent catalytic action was manifest even when only a small amount of it was incorporated into the surface layer of tin dioxide, which is a considerably less active catalyst [19]. In more detailed studies the vapour phase decomposition of perchloric acid has been investigated with all oxides already studied in the decomposition and combustion of ammonium perchlorate [20, 21]. The experiments were carried out in a flow system using N_2 as carrier gas.

Depending upon the nature of cations, oxides catalyze the decomposition of perchloric acid vapour in different temperature ranges. The chemical analysis of the gaseous products revealed that the decomposition of perchloric acid on most of the catalysts takes place according to the process:

$$2\,HClO_4 = Cl_2 + H_2O + 3.5\,O_2 \tag{40}$$

The reaction

$$HClO_4 = HCl + 4\,O_2 \tag{41}$$

occurred only to a limited extent. A considerable amount of ClO_2 was found, however, on chromium oxide, which decomposed perchloric acid at temperatures as low as 130 °C.

The amount of chlorine dioxide increased from 130 °C to 155 °C; above 160 °C, however, it suddenly decreased. This observation suggests that Eq. (40) reflects only the end-state of the reaction on other oxides, and that the unstable chlorine oxides formed during the reaction decompose into chlorine and oxygen either on the catalyst or in the heated reactor space. The initial activities (in terms of percentage conversion) of the catalysts generally decreased after the first few measurements; however, in the later stages they remained practically constant (Fig. 7). On Cr_2O_3, below 160 °C, a slight decrease in activity was noticed. Above 170 °C, however, activity decreased gradually, and no constant activity was reached even after several hours. In the temperature range of AP decomposition, *i. e.* between 200 and 350 °C, the decrease in activity was so pronounced that after a reaction time of 2 hours the activity measured at 260 °C was lower than at 180 °C.

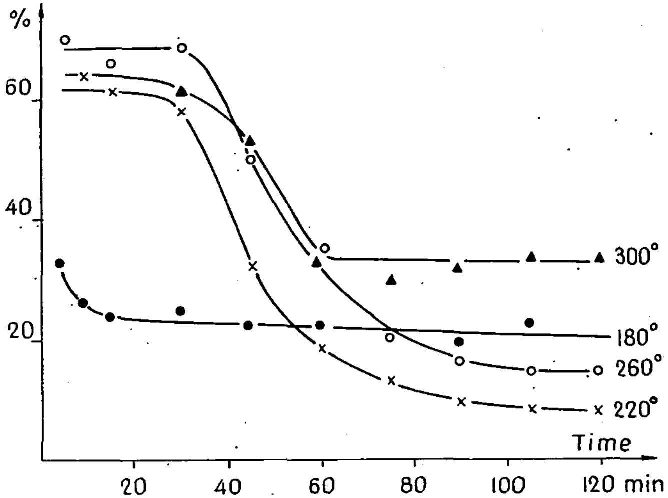


Fig. 7. Change in the catalytic activity of Cr_2O_3 at higher temperatures. The points indicate the percentage decomposition of $HClO_4$ at different stages of pretreatment [18].

Interaction between the catalyst and perchloric acid [21—25]

In order to get a closer insight into the nature of the interaction between perchloric acid and the catalyst, electric resistivity, infrared spectroscopy and differential thermal and chemical analyses were carried out. The electric resistivities of the oxides in the presence of perchloric acid were measured at the temperature of the catalytic reaction and whenever possible at about 80 — 100 °C lower temperatures. In the latter case the change in resistivity was probably due to the effect of the perchloric acid, whereas in the first case the effect of the decomposition products could also have played a part. A particularly great change in resistivity was observed in the case of Cr_2O_3. As can be seen in Fig. 8, perchloric acid reduced the resistivity of Cr_2O_3 and the decrease was greater at lower temperatures. The change in resistivity occurred within a few minutes and afterwards altered only slightly. When the gas containing perchloric acid was replaced by pure nitrogen, the resistivity of Cr_2O_3 was little affected, indicating that the surface of the catalyst (due to the oxidative properties of the gaseous species) underwent an irreversible change during the catalytic reaction.

Chemical analysis of Cr_2O_3 catalysts revealed that the substance is oxidized during the catalytic reaction. The degree of oxidation increased as the temperature of perchloric acid treatment was raised from 120 °C to 220 °C. A sudden increase in the rate of oxidation occurred at 170 °C. Above 220 °C the active oxygen content of Cr_2O_3 decreased, which might be attributed to the evaporation of CrO_2Cl_2 and CrO_3. Fig. 9 shows the relation between the electric properties and the active oxygen content of Cr_2O_3 treated with $HClO_4$ at various temperatures.

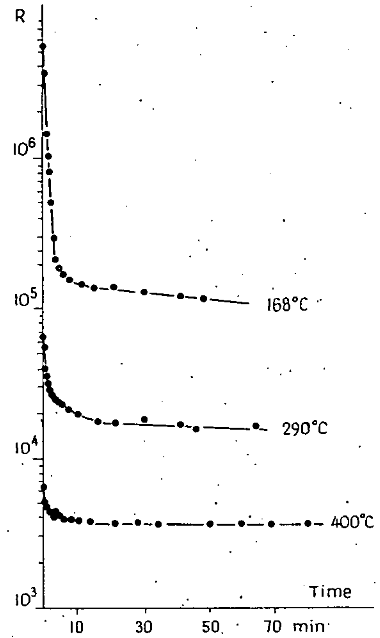


Fig. 8. Changes in the electric resistivity of chromium oxide in the presence of perchloric acid vapour at different temperatures [20].

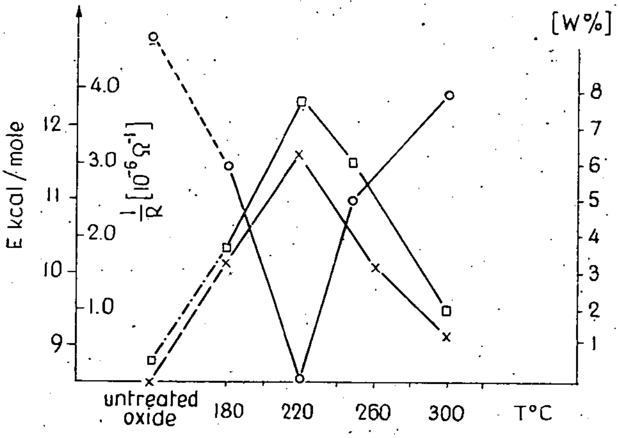


Fig. 9. Electric conductivity of Cr_2O_3, □; activation energy of electric conductivity, O; and active oxygen content of chromium oxide, X; as functions of the pretreatment temperature with perchloric acid [22].

In one case, at 170 °C, the increase in the active oxygen content in the chromium oxide was followed simultaneously with the activity of the catalyst. For this purpose, a fresh catalyst was used in each run, and the weight increases and active oxygen contents of the catalysts were determined after a certain time. Thus, the values for each reaction time were determined on separate samples.

The active oxygen content of chromium oxide increased with increasing reaction time; however, after 180 min only a slight change was observed and the saturation value was finally reached. At this stage the active oxygen content of the catalyst was about 3.7% by weight. It was also observed that the amount of decomposed perchloric acid was not directly proportional to the reaction time, probably because of the change occurring in the composition of the catalyst.

Thermogravimetric and differential thermal analyses have shown that Cr_2O_3 treated below 200 °C loses its excess oxygen in an endothermic process in two stages between 360° and 470 °C.

A similar type of surface oxidation was observed on nickel oxide when the active oxygen content increased from 0.069% to 0.133% at 260 °C after a reaction time of 2 hours [24].

Electric conductivity measurements indicated a considerable interaction between perchloric acid and zinc oxide [21]. At the temperature of the catalytic decomposition of perchloric acid (350°) the conductivity of zinc oxide measured in nitrogen decreased by about 4 orders of magnitude within a few minutes, after which, however, there was no or only a slight change.

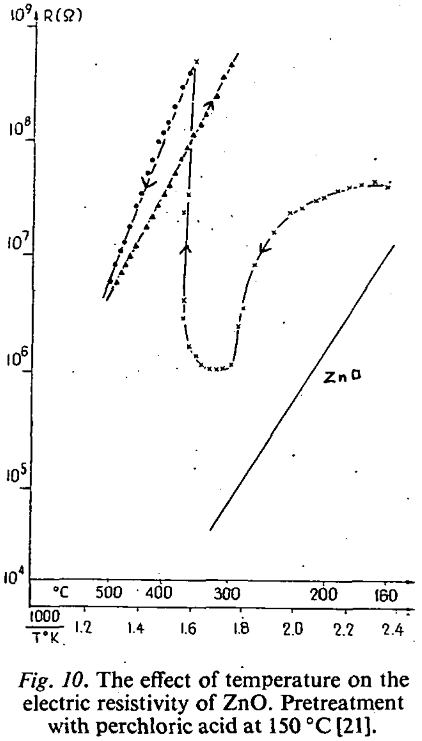


Fig. 10. The effect of temperature on the electric resistivity of ZnO. Pretreatment with perchloric acid at 150 °C [21].

When the nitrogen gas containing perchloric acid was replaced by pure nitrogen, the initial state could not be reestablished, and only a minimal increase in conductivity occurred. However, on the effect of NH_3, the initial resistivity value was reached within a few minutes. This observation reveals that the excess zinc in the surface layer of zinc oxide undergoes an irreversible oxidation due to the perchloric acid and/or its decomposition products.

The adsorption of perchloric acid had considerably less influence on the electric conductivity of ZnO at 150°. In 30 min 1.06 mg of $HClO_4$ was irreversibly adsorbed on 1 g of zinc oxide. An interesting behaviour was observed when the oxide treated with $HClO_4$ at 150 °C was heated to higher temperatures in pure nitrogen. Electric resistivity decreased up to 330 °C — which corresponds to the temperature of the catalytic reaction — then suddenly increased by about 2—2.5 orders and on further heating decreased again. This behaviour can be explained by taking into account that at 330° chemisorbed perchloric acid decomposes and simultaneously the surface of zinc oxide becomes oxidized, leading to greatly increased resistivity. The results of these experiments are shown in Figure 10. For the sake of comparison the dependence of the electric resistance of untreated, regularly behaving zinc oxide is also shown.

The behaviour of the other oxides in perchloric acid vapour depends upon their semiconductor nature. *p*-Type semiconductors followed the pattern of Cr_2O_3 and the *n*-type ones behaved like ZnO [20]. These results indicate that the chemisorption of $HClO_4$ on the oxides is very probably an acceptor process.

Kinetic investigations

The kinetics of the catalytic decomposition of perchloric acid has been investigated in a flow system. In the range of 0.5 to 8% conversion per minute, catalytic decomposition in most cases followed first order kinetics, which means that the slowest step on the catalyst is probably the chemisorption of $HClO_4$.

A notable exception is Cr_2O_3, on which the reaction was found to be of zero order. In this case the rate determining step may be the decomposition of the perchlorate ions on the surface. Some Arrhenius diagrams of the rate constants are shown in Fig. 11.

The apparent activation energy was also calculated in every case and was found to lie in the range of 25 to 45 kcal/mole.

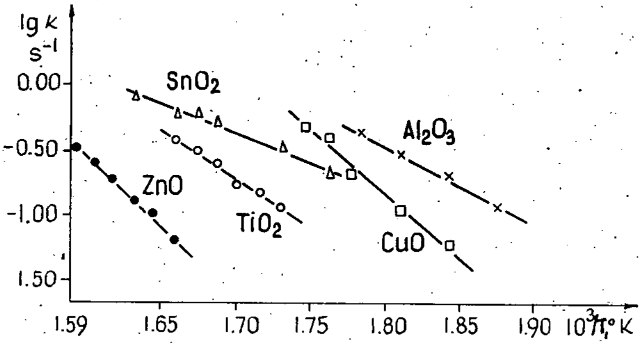


Fig. 11. Arrhenius diagrams of first order rate constants [20].

Kinetic data are shown in Table IV. When considering the efficiency of the oxides in the decomposition of perchloric acid, the temperature range of the reaction and the first order rate constants at 300 °C were taken into account. Accordingly, the catalysts can be divided into three groups;

a) Highly effective oxides which have a significant catalytic action even at 130 °C (Cr_2O_3) and in the range between 240 and 290 °C (cobalt, nickel, copper(II), iron(III) and aluminium oxides).

b) Fairly effective oxides (stannic, titanium, zinc oxides) which catalyze the decomposition of perchloric acid between 300 and 360 °C.

c) Inactive oxides (cadmium, magnesium, calcium oxides) in the presence of which there is no detectable catalytic reaction.

Table IV

Kinetic data of the catalytic decomposition of perchloric acid

Catalyst	Surface areas m²/g	Reaction temperature °C	k_{spec} (s^{-1} m^{-2}), at 300 °C	Activation energy kcal/mole	Specific pre-exponential factor ($min^{-1}m^{-2}$)	Conversion at 300 °C m^{-2}	References
Cr_2O_3	1.50	150—180		31.0		39.8 (180°)	[20]
NiO	4.22	210—250	3.9585	27.1		9.7 (250°)	
CuO	0.435	270—300	1.4350	42.8		38.3	
Co_2O_3— —Co_3O_4	12.8	210—260	(1.4)	—		20.5	
Fe_2O_3	5.52	250—285	0.5831	42.6		20.2	
Al_2O_3	8.41	240—290	0.2942	26.5		10.6	
SnO_2	2.76	295—340	0.2220	20.7		5.8	
TiO_2	8.20	305—330	0.0350	33.0		0.86	
ZnO	1.64	330—355	0.0154	45.6		0.40	
CdO	7.00	400	—	—		—	
MgO	4.95	400	—	—		No decomp.	
SiO_2	9.64	400	—	—		No decomp.	
CaO	1.95	400	—	—		No decomp.	
$CuCr_2O_4$	7.5	115—150		17.0			[27]
		115—150		26.0			
$CuCrO_4$	21.1	330—355		32.0			
Harshaw Cu —0202 (78% CuO 20% Cr_2O_3)	23.2	200—240		28.0			
Harshaw catalysts							
Cu—0203 (78% CuO 20% Cr_2O_3)	12.5	185—261		54.0	$2.5 \cdot 10^{22}$		[31]
Fe—0301 (20% Fe_2O_3 on Al_2O_3)	41.0	177—238		28.6	$2.5 \cdot 10^{10}$		
Cu—8803 (10% CuO on Al_2O_3)	13.7	196—250		39.0	$8.0 \cdot 10^{14}$		
Al—0104 (99% Al_2O_3)	80.0	176—251		28.8	$1.3 \cdot 10^{10}$		
Mn—0201 (19% MnO_2 on Al_2O_3)	69.0	142—207					

For the evaluation of the factors which determine the catalytic effects of metal oxides, the perchlorate salts of the relevant metal ions were prepared and their thermal stabilities studied [23]. This included the determination of their decomposition temperatures and that of the reaction products, as well as the kinetic decomposition data. In Table V. the perchlorate salts are given in the order of their stabilities, together with the temperature ranges and products of decomposition. When comparing the catalytic influence exerted by the metal oxides on the decomposition of perchloric acid with the thermal stabilities of the corresponding perchlorates, a close relationship appears, namely the most active oxides lead to the most unstable perchlorates. Thus, it was concluded that the catalytic decomposition of perchloric acid takes place through the formation and decomposition of perchlorate ions on the surface of the catalyst.

Table V

Thermal decomposition of metal perchlorates [23]

Substance	Temp. range of decomposition, °C	Decomposition products
$Cr(ClO_4)_3$	135—160	Cr_2O_3, ClO_2, Cl_2, O_2
$Co(ClO_4)_2$	195—265	$Co_2O_3+Co_3O_4$, Cl_2, O_2
$Ni(ClO_4)_2$	245—290	NiO, $(NiCl_2)$, Cl_2, O_2
$Cu(ClO_4)_2$	245—290	CuO, $(CuCl_2)$, Cl_2, O_2
$Al(ClO_4)_3$	260—300	Al_2O_3, Cl_2, O_2
$Fe(ClO_4)_2$	280—315	Fe_2O_3, Cl_2, O_2
$Zn(ClO_4)_2$	285—310	ZnO, $(ZnCl_2)$, Cl_2, O_2
$Cd(ClO_4)_2$	377—403	$CdCl_2$, O_2
$Mg(ClO_4)_2$	386—405	MgO, $MgCl_2$, Cl_2, O_2
$Ca(ClO_4)_2$	400—422	$CaCl_2$, O_2

Decomposition of perchloric acid on propellant catalysts and on their components, copper chromite and chromate

The thermal decomposition of perchloric acid has been studied also on mixed oxides which are actually used as a composite propellant catalysts [26—29]. Depending upon their origin these catalysts may have different compositions. The compositions of the most frequently used catalysts are shown in Table VI.

According to these data, two basic types can be distinguished: one consists of copper chromite and the other of copper chromate, but both types of catalysts also contain significant amounts of free copper oxide.

The decomposition of perchloric acid on the Harshaw Cu — 0203 catalyst was observed above 180 °C. The reaction products were: Cl_2, O_2 and H_2O (reaction (40)). During the conditioning period also HCl was formed. At higher temperatures the activity of the catalyst decreased suddenly and constant activity was reached only after a fairly long conditioning period.

Of the components of composite propellant catalysts, cupric chromite was found to be the most effective. The perchloric acid decomposed on cupric chromite even at 120 °C. The catalytic reaction proceeded according to the reaction (40).

During the conditioning period 5—10% of hydrogen chloride was also found; this amount, however, decreased as a function of time. Below 160 °C a few percent of ClO_2 too was also detected in the decomposition products. The activity of the

Table VI

Sources, nominal formulas and compositions of propellant catalysts

Catalyst	Source Nominal Formula
Copper chromate	Propellant grade $CuCrO_4 \cdot 2\,Cu(OH)_2$ Cu as CuO 62%; Cr as CrO_3 28%
Copper chromate	Hopkins Williams, Ltd. $CuCrO_4 \cdot 2\,Cu(OH)_2$
Copper chromate	Harshaw Chemical Co. Harshaw Catalyst Cu 0202 p Cu as CuO 82%; Cr as Cr_2O_3 17%
Copper chromite	Research Inorg. Chem. Co. 99%
Cupric oxide	Hopkins Williams, Ltd. CuO "Analar" grade

cupric chromite varied only slightly below 145 °C, but a large activity decrease occurred above 180 °C. On the action of perchloric acid the colour of the catalyst changed from black to brown, indicating the oxidation of the latter.

Cupric chromate proved a substantially poorer catalyst of the decomposition of perchloric acid than the former substances. In fact a catalytic reaction was observed only above 330 °C. The activity of the chromate became constant after about 30—40 min. The catalytic reaction proceeded according to the equation (40).

On the basis of the above results the loss of activity of cupric chromite was attributed to its oxidation and to the formation of a much less active chromate [26—28]. Recently GILBERT and JACOBS [31] observed that in the case of the Harshaw Cu—0203 catalyst initially all the perchloric acid which passed over the catalyst at about 260 °C was consumed and catalytic decomposition could be observed only after a few runs. The activity of the catalyst then increased to more than ten times its original value. They postulated that the cupric chromate formed during the conditioning period functioned as the actual catalyst which is in disagreement with the above conclusion. When the individual properties of the components of the Harshaw catalyst as well as its cupric oxide content (~80%) are considered, it seems more likely that the cupric oxide and not the cupric chromate acted as catalyst at the above temperature. It cannot be excluded, however, that the partially oxidized chromate also contributed to the measured activity value. Since GILBERT and JACOBS used an extremely large amount of catalyst (~30 g), it is likely that catalytic decomposition in the conditioning period was precluded by a chemical reaction between the catalyst and perchloric acid. The catalytic effect of cupric oxide (and that of partially oxidized chromite) could be exhibited only when the oxidation of the highly reactive chromite had proceeded to a certain extent.

The interactions between the catalysts and the perchloric acid have been studied in a similar way as in the case of single oxides [27, 28].

In the presence of perchloric acid a significant weight increase (~ 5%) of cupric chromite occurred at the lowest temperature used in the investigation, *i.e.* at 120 °C. The extent of weight-increase increased with time and also with temperature up to 150 °C. A reversible physical adsorption was observed only below 140 °C, but its contribution to the weight increase never exceeded 10%. Below this temperature weight increase was caused mainly by the chemisorption of perchloric acid, *i.e.* the formation of surface perchlorate ion. A slight oxidation of chromite can also be detected in this temperature range. Above 160 °C the decomposition of surface perchlorate was so fast than even its transitory presence was not detectable with infrared analyses. A larger band, however, belonging to the CrO_4^- anion, appeared on the infrared spectra.

Chemical analyses of the catalysts also indicated that above 160 °C the surface oxidation of the catalyst came into prominence.

The electric resistivity of cupric chromite decreased in the presence of nitrogen gas containing perchloric acid, which can be attributed to the acceptor-type chemisorption of the perchloric acid and the surface oxidation of the catalyst, and hence to the increase of the excess oxygen content of the electron-hole conducting (*p*-type) cupric chromite.

The behaviour of the Harshaw catalyst showed the characteristics of both cupric chromite and oxide. The oxidation of the chromite content was detected as low as 140 °C. The formation of surface perchlorate ion was established from 125 to 245 °C.

In contrast to the previous catalysts, cupric chromate adsorbed perchloric acid even above 300 °C and the adsorbed perchloric acid decomposed only above 340 °C. This indicated a high stabilization of adsorbed perchloric acid due to chromate ion. This observation is in agreement with the previous finding, namely that the decomposition of perchloric acid on cupric chromate is negligible below 300 °C. In spite of the presence of a large amount of perchloric acid the electric resistivity of cupric chromate changed only very slightly.

When the catalyst was pre-treated with perchloric acid to constant activity, the decomposition of perchloric acid followed first order kinetics at 115—150 °C. The value of activation energy was 17 kcal/mole. Taking into account that, especially at higher temperatures, the surface oxidation of cupric chromite is significant, which may influence the obtained kinetic data, the activation energy was also determined from the temperature dependence of the initial reaction rate. In order to minimize further the effect of activity changes, at each temperature a fresh catalyst was used on which three measurements were taken made for 15 min. In this way a value of 26 kcal/mole was obtained for the activation energy.

First order kinetics were valid in the case of the Harshaw catalyst in the temperature range 200—240 °C. The activation energy was 28 kcal/mole. No change in the value of activation energy was found when it was calculated from the temperature dependence of the initial rate using a fresh catalyst at each temperature.

The rate of decomposition on cupric chromate at 330—355 °C was practically independent of the partial pressure of perchloric acid, which indicated zero order kinetics. The value of the activation energy was 30 kcal/mole [27, 28] (Table IV).

The high initial catalytic activity of the catalysts containing cupric chromite was attributed to the instability of the surface perchlorate ion bonded to the chromium(III) ion.

Recently GILBERT and JACOBS [31] carried out kinetic investigations on the decomposition of perchloric and on five Harshaw catalysts: copper chromite, alumina, iron(III) oxide, copper(II) oxide and manganese(IV) oxide (Table IV). The interaction between the catalyst and perchloric acid was not studied and neither adsorption nor infrared spectroscopic measurements were made.

Manganese(IV) oxide gave complex kinetics which were not fully analyzed, but on the other four catalysts the reaction was also found to be first order. Evaluation of the results was complicated by the fact that the iron, copper and manganese oxide were not pure substances but were supported on alumina. This latter, as has already been shown, is also an active catalyst for the decomposition of perchloric acid so it is difficult to judge the intrinsic activity of the single oxides. The catalytic decomposition of perchloric acid was also described by the formation and decomposition of surface perchlorate ions.

From the point of view of the detailed mechanism of the catalytic decomposition of perchloric acid it is very important to determine its primary products. Since these species are highly reactive and decompose very easily, the conventional analytical methods cannot be used for this purpose. In principle mass spectrometric analysis seems suitable, but the fragmentation of perchloric acid due to electron impact introduces a considerable difficulty into the qualitative assessment of the reaction products. As has been shown before, field ionization of perchloric acid on Pt emitter proceeds under certain conditions practically without significant fragmentation [16]. As a continuation of this work SOLYMOSI and BLOCK [32] investigated the possibilities of the application of field ionization mass spectrometry to the analysis of the primary products of the catalytic decomposition of perchloric acid on cupric oxide.

A micro-catalytic reactor was incorporated into the field ion source. The perchloric acid vapour and its decomposition products entered the ionization chamber provided with a Pt-emitter about 5 mm in front of the reactor.

The intensity of $HClO_4^+$ ions and that of the total ion current was practically constant at $T_R=25$—120 °C (T_R=reactor temperature) and with a tip temperature T_t slightly above room temperature. Some fragment ions appeared even at $T_R=25$ °C which are due to a slight instability of the parent molecular ion. The relative intensities of the ions of chlorine oxides, such as ClO, ClO_2, ClO_3 and ClO_4, were an low level of about 1% but somewhat higher than the values due to the field fragmentation on a Pt-emitter (in other words, without catalysts). A decrease in the intensity of $HClO_4^+$ ion due to the decomposition was observed only above 120 °C. The onset of decomposition was indicated more sensitively by the increased intensity of the ClO_2^+ ion, which was the main chlorine oxide product of the catalytic reaction. The ion current of the ClO_2^+ ion was doubled even at 100 °C and increased markedly with the increase of T_R. The intensities of the ClO_2^+ ion at different temperatures are plotted in Fig. 12.

The intensity of the ClO_3^+ ion decreased when the decomposition started; its ratio to the $HClO_4^+$ ion was practically constant between $T_R=25$—215 °C indicating that the ClO_3^+ ion is probably not being formed in the catalytic decomposition of $HClO_4$.

A slight increase in the intensity of ClO^+ and Cl_2^+ ions occurred at the decomposition temperature of $HClO_4$, at $T_R=120$ °C, and it remained at constant level up to $T_R=285$ °C. Their relative intensity to $HClO_4^+$ ion gradually increased with the temperature above $T_R=120$ °C. The fact that the ratios ClO^+/ClO_2^+ and

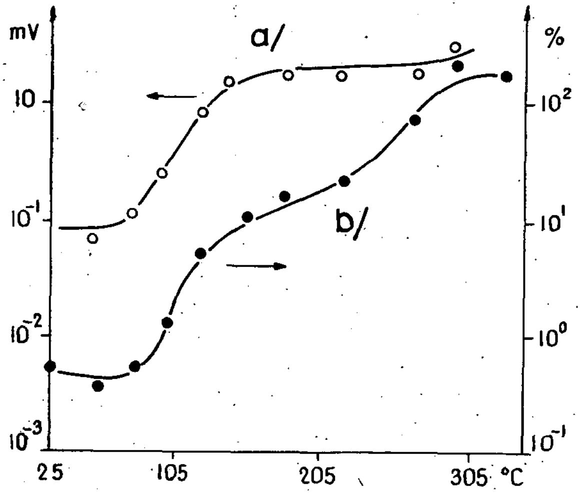


Fig. 12. Absolute and relative intensities of ClO_2^+ ions at different temperatures [32].

Cl_2^+/ClO_2^+ do not vary with temperature indicates that these species are not the products of decomposition of ClO_2.

From these results it was concluded that the mechanism of decomposition of $HClO_4$ on CuO catalyst is different from that of homogeneous decomposition where the primary step is the rupture of the HO—Cl bond yielding ClO_3 and OH radicals

$$HO{-}ClO_3 = OH + ClO_3. \tag{42}$$

This study supported the idea suggested before that the first step in the catalytic decomposition is the dissociative chemisorption of $HClO_4$ on the oxide surface

$$H^+ClO^-_{4(g)} = H^+_{(ads)} + ClO^-_{4(ads)}. \tag{43}$$

This is probably followed by the bimolecular decomposition of surface perchlorate ion

$$2\,H^+_{(ads)} + 2\,ClO^-_{4(ads)} = H_2O_{(g)} + 2\,ClO_2 + \frac{3}{2}\,O_2. \tag{44}$$

In a minor step, the decomposition of surface ClO_4^- ion yields ClO and Cl_2, too. The appearance of ClO_4^+ ion in the field ion mass spectra may also prove the dissociative adsorption of $HClO_4$. The intensity of ClO_4^+ ion is very low indeed, but one should keep in mind that to turn the ClO_4^- ion into a positive ion requires stripping off an electron pair

$$ClO_4^- \xrightarrow{-2e} ClO_4^+ \tag{45}$$

which is not an easy process to occur. The intensity of ClO_4^+ ion gradually increases with the temperature up to 100 °C, suggesting the occurrence of activated adsorption of $HClO_4$. At 120 °C, when the decomposition sets in, the intensity of ClO_4^+ begins to decrease and disappears at higher temperatures.

Reactions between perchloric acid and simple fuels

From the point of view of understanding the processes occurring in the combustion of propellants based on ammonium perchlorate, it is very important to be acquainted with the nature of the reactions between perchloric acid and different fuels. Jacobs *et al.* [33—36] investigated the slow reactions between diluted perchloric acid and various simple fuels (hydrogen, methane, ethane and ethylene) in a flow system. In the presence of hydrogen the reaction was faster at all temperatures between 143 and 417 °C than the decomposition of the acid alone [33, 34]. The reaction appeared to be roughly of the first order. The only chlorine containing product was hydrogen chloride; no oxygen was detected by means of gas chromatography. Reproducibility was improved after continued use of the reaction vessel coated with boric acid. The following mechanism was first suggested for the reaction between hydrogen and perchloric acid [33]:

$$H_2+HClO_4 = H_2O+ClO_2+OH \tag{46}$$

$$OH+H_2 = H_2O+H \tag{47}$$

$$H+ClO_2 = OH+ClO \tag{48}$$

$$H+ClO = OH+Cl \tag{49}$$

$$Cl+H_2 = HCl+H. \tag{50}$$

If the view of the work of Clyne [37], however, who found no detectable reaction of H atoms with $HClO_4$ at 127 °C in a discharge flow system, the above mechanism has been modified and the dissociative chemisorption of H_2 was proposed as an initial step:

$$H_2+S\,(\text{surface}) \rightarrow S{-}H+S{-}H \tag{51}$$

$$S{-}H+HOClO_3 \rightarrow S+H_2O+ClO_3. \tag{52}$$

The gas-phase reaction of perchloric acid with methane was studied between 297 and 413 °C in a flow system [36]. The only major chlorine containing major product was hydrogen chloride. In the absence of methane the decomposition of $HClO_4$ resulted in Cl_2 only. Oxygen and a small amount of carbon monoxide were also found. Gas chromatographic analysis revealed the formation of CH_3Cl, CH_2Cl_2, $CHCl_3$ and CCl_4.

As the rate of formation of HCl was equal to the rate of formation of Cl_2 in the absence of methane, it was inferred that the presence of methane exerted no influence upon the decomposition of $HClO_4$ and the methane reacts only with products of decomposition of $HClO_4$. Taking into account the reactivity of molecular oxygen, ClO, Cl, O and OH radicals towards methane, it was proposed that Cl atoms are responsible for the consumption of methane in the reacting system.

However, reconsidering the analytical data Jacobs and Stevenson [35] pointed out that the HCl produced is a measure of only about half the total perchloric acid decomposed, as the Cl_2 produced by the decomposition of acid is converted to HCl and CH_3Cl in the reaction with CH_4. This implies that the methane does influence the decomposition of $HClO_4$; it reacts with acid directly, or some intermediate formed in the CH_4+HClO_4 reaction attacks the $HClO_4$.

The rate increasing effect of organic fuel in the decomposition of $HClO_4$ was clearly demonstrated recently in the case of the gas-phase reaction of perchloric acid with ethylene [35] (Fig. 13). At 320 °C the decomposition of $HClO_4$ was faster by a factor of 2 in the presence of ethylene.

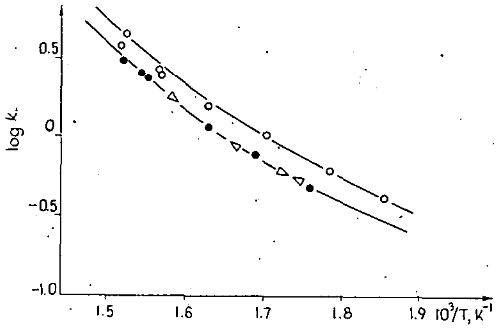
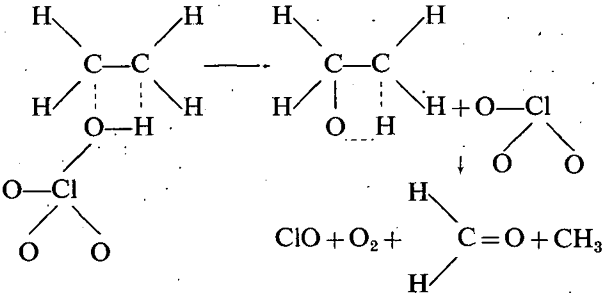


Fig. 13. Comparison of the rate data of the $HClO_4+C_2H_4$ system with those of the corresponding $HClO_4+CH_4$ system. ● $HClO_4+CH_4$; △ $HClO_4$ alone (in methane series); $HClO_4+C_2H_4$; ▽ $HClO_4$ alone (ethylene series). The lower continuous line was obtained by the computer and fitted to the data assuming that they represent the sum of two first order reactions [35].

The Arrhenius diagrams were curved in both the absence and presence of fuel (Fig. 13). This was explained by the occurrence of two parallel reactions; the high temperature homogeneous and the low temperature heterogeneous decomposition of $HClO_4$. The major products were hydrochloric acid, carbon monoxide and water. The most important organic products were 1,2-dichloroethane and vinyl chloride.

For the accelerated decomposition of $HClO_4$ in the presence of ethylene a direct molecular reaction between the two compounds is suggested involving the following transition state



(53)

(54)

The other possibility is the reaction of $HClO_4$ with radicals (vinyl, HO_2 or CH_2Cl) formed in the $C_2H_4+HClO_4$ system. At present no final choice can be taken between the different alternatives.

Effects of catalysts

Pearson [38] has shown that alternate exposure of Harshaw Cu—0202 to various fuels (ethylene, iso-butene, ammonia) and to oxygen at 400° to 420 °C resulted in the alternate reduction and oxidation of the catalyst. Both stages of the redox cycle were exothermic reactions. No redox cycle was observed when methane was used as fuel. Since the percentage weight changes were independent of the sample weight and of the nature of the fuel, it was assumed that the bulk of the catalyst was reduced.

Alternate exposure to isobutene and perchloric acid induced a similar redox cycle, but for a net weight gain of the catalyst after exposure to perchloric acid. The surface layer of chromite changed its colour from black to a mottled reddish brown. This weight gain was attributed partly to the oxidation of Cr(III) to Cr(VI) and partly to the formation of unreactive copper chloride or oxychloride.

It has been concluded that the enhanced heat release from the oxidation-reduction processes on catalyst particles constitutes one way of raising the burning rate of composite propellants.

Perchloric acid decomposition flame

The decomposition flame of perchloric acid vapour in the absence of fuel has been observed at 400° to 405 °C [10]. In the presence of hydrogen ignition occurred practically at the same temperature, while platinum reduced the ignition temperature to 390 °C only. A significant catalytic effect was observed in the presence of steel, when ignition occurred at 215 °C, just above the boiling point of 72% perchloric acid.

The perchloric acid decomposition flame was studied in more detail by Cummings *et al.* [39, 41]. The flame was stabilized using the vapour from aqueous perchloric acid (72%). The measured burning rate and temperature agreed with the computed values when allowance was made for the non-equilibrium distribution of chlorine in the product gases. The activation energy for the decomposition flame was close to 45 kcal/mole and the overall activation energy deduced for the premixed H_2—$HClO_4$ flames was 15 kcal/mole. The first value was in agreement with the value of the decomposition of $HClO_4$ vapour which was associated with the fission of the HO—ClO_3 bond. From these data it was concluded that the acid dissociation controls the decomposition flame but does not determine the burning rate of fuel- perchloric acid premixed flames.

In the subsequent studies Pearson *et al.* revealed the characteristics of premixed flames of $HClO_4$ with methane, ethane and ethylene [40—47]. The burning rates of mixed flames considerably exceeded those supported by oxygen and the corresponding fuel. In the case of methane, carbon dioxide formation occurred earlier than in an oxygen flame [40, 41]. The addition of oxygen to a slightly rich flame produces a second reaction zone downstream of the first. This second zone is characteristic for methane—oxygen flames. From a more detailed study of the two-flame formation in the presence of added oxygen it appeared that most of the added oxygen reacts in the perchloric acid flame and results—probably through an enhanced production of ClO—in an increased consumption of methane [42]. The emission spectra of methane-perchloric acid flames showed "cool-flame" bands. The higher reactivity of $HClO_4$ in the oxidation compared to molecular oxygen was attributed to the ClO radical formed in its decomposition. In the proposed mechanism the following reactions are the principal ones:

$$HClO_4 \rightarrow OH + ClO_3 \tag{55}$$

$$ClO_3 \rightarrow ClO + O_2 \tag{56}$$

$$CH_4 + ClO \rightarrow CH_3 + HOCl \tag{57}$$

$$OH + HOCl \rightarrow H_2O + ClO \tag{58}$$

$$CH_3 + ClO \rightarrow CH_2O + HCl \tag{59}$$

$$CH_3 + O_2 \rightarrow CH_2O + OH \tag{60}$$

$$CO + ClO \rightarrow CO_2 + Cl \tag{61}$$

$$CO + OH \rightarrow CO_2 + H. \tag{62}$$

The main step is the consumption of methane by the ClO radicals. The reaction involves sufficient energy to excite formaldehyde and to account for the observed "cool- flame" bands.

In perchloric acid flames rich in methane only two moles of methane reacted with one mole of perchloric acid; the rest acted as a diluent. In the case of ethylene, and acid flames rich in ethane 3 and 3.5 moles of fuel were consumed per mole of acid [43, 44]. The formation of carbon was observed and it was assumed that more than two fuel molecules were consumed by side reactions and by pyrolysis.

In Table VII some pertinent data of the perchloric acid flames rich in fuel are shown [44].

The following general mechanism is suggested for perchloric acid flames rich in fuel

$$HClO_4 \rightarrow HO + ClO_3 \tag{63}$$

$$ClO_3 \rightarrow ClO + O_2 \tag{64}$$

$$ClO + RH \rightarrow R + HOCl \tag{65}$$

$$H + HOCl \rightarrow H_2O + Cl \tag{66}$$

$$Cl + RH \rightarrow R + HCl \tag{67}$$

$$R + O_2 \rightarrow CO + \text{products} \tag{68}$$

$$H + HClO_4 \rightarrow H_2O + ClO_3 \tag{69}$$

$$2\,R \rightarrow R_2 \tag{70}$$

$$R \rightarrow \text{decomposition} \tag{71}$$

Table VII

Fuel-perchloric acid mixtures near upper flammibility limit

Fuel	% Fuel	Mixture ratio	Temperature K	Burning rate cm s^{-1}
Methane	84	20	1070	13
Ethane	76	22	1050	10
Ethylene	86	31	1050	10

Later work on fuel—rich perchloric acid flames containing mixed hydrocarbons (methane—ethane, methane—ethylene and ethane—ethylene) revealed that one member of each fuel pair is selectivly consumed [45]. Resistance to attack increases in the order ethane<ethylene<methane. Comparison of this order to that of the burning rates indicated that methane burns appreciably faster than ethylene or ethane. From the comparison of the approximate ratios of the rate constants deduced with the help of published values of the reaction of the same compounds with O, H, Cl atoms and OH radicals it appeared that the important components of the perchloric acid flames are chlorine—oxygen radicals and not those (H, O and OH) which are significant in oxygen flames. Tentative activation energies have also been derived for the reaction of methane and ethane with reactive species.

The formation of two methane-perchloric acid flames has also been observed in the absence of added oxygen in flames containing an appreciable amount of diluent (N_2 or Ar) [46]. In this case the second flame results from the combustion of carbon monoxide and of small amounts of hydrocarbon not oxidized in the first flame. It has been suggested that perchloric acid has a dual oxidizing action; it provides a highly reactive chlorine—oxygen species and oxygen.

It is an interesting fact that ClO_2—CH_4 flames have at low pressure many similarities to the perchloric acid flames [47]: (*i*) there are very intense "cool—flame" bands (excited formaldehyde) in the emission spectrum, (*ii*) if oxygen is added to a flame rich in methane the second flame appears downstream of the first one, (*iii*) and the burning rates of CH_4—ClO_2 and CH_4—$HClO_4$ mixtures are virtually the same when the stoichiometry and the final flame temperature are the same.

The values of the overall activation energies for several flames are given in Table VIII. Both ClO_2 and $HClO_4$ flames have much lower activation energies than the 50 to 60 kcal/mole calculated for methane-oxygen flames [48, 49]. The small difference in the activation energies of the stoichiometric mixtures of ClO_2 and $HClO_4$ is probably due to the different steps in their initial decomposition. From the general similarity between methane flames containing chlorine dioxide and perchloric acid it seemed reasonable to conclude that ClO_2—CH_4 and $HClO_4$—CH_4 flames involve basically the same reaction steps.

In the case of ClO_2 the radicals are produced initially by the decompositions

$$ClO_2 \rightarrow ClO + O \quad +58.8 \text{ kcal/mole} \tag{72}$$

$$O + ClO_2 \rightarrow ClO + O_2 \quad -60.4 \text{ kcal/mole.} \tag{73}$$

Table VIII

Activation energies of methane flames with chlorine dioxide, perchloric acid and oxygen [49].

Oxidizer	λ	Diluent	Activation energy kcal mole^{-1}
ClO_2	1.6	Ar, N_2	14.8
$HClO_4 \cdot 2.17\ H_2O$	1.0	N_2	23.8
	1.5	N_2	20.7
	2.0	N_2	22.6
	2.0	Ar	15.7
	2.0	CH_4	23.3
O_2	1.0	N_2	50.6
	1.64	N_2	60.7
	2.0	N_2	61.7

In the propagating flame these may be replaced by reactions such as

$$O + ClO_2 \longrightarrow ClO + O_2 \quad -60.4\ \text{kcal/mole} \tag{74}$$

$$Cl + ClO_2 \longrightarrow ClO + ClO \quad -5.5\ \text{kcal/mole} \tag{75}$$

since the studies of CLYNE and COXON (37, 50] revealed that in these processes ClO radicals are readily formed. These steps would then be followed by the same series of reactions as in the case of the $HClO_4$—CH_4 system.

In the flames of both systems the key role is played by the ClO radical due to its high dissociation energy (45 kcal/mole), its slow bimolecular recombination (10 to 10^8 liter$\cdot$mole$^{-1}\cdot$s^{-1}) and to the fact that ClO is a major product of the thermal decomposition of $HClO_4$.

The kinetic studies of ClO-radical reactions in a discharge — flow system raise some doubt, however about the dominant role of the ClO radical. CLYNE and COXON [37, 50, 51] found that the ClO radical does not react with H_2 at 300 K. The upper limit for the rate constant (k_1) of the reaction

$$ClO + H_2 \xrightarrow{k_1} \text{products} \tag{76}$$

was at this temperature $10^{8.5}$ cm$^3\cdot$mole$^{-1}\cdot$s^{-1}. Instead of a direct reaction between ClO and H_2 a chain reaction taking place quite rapidly even at room temperature is supposed, with atomic chlorine as the chain carrier

$$Cl + H_2 \longrightarrow HCl + H \tag{77}$$

$$H + ClO \longrightarrow HCl + O \tag{78}$$

$$O + ClO \longrightarrow Cl + O_2. \tag{79}$$

CLYNE has extended his studies to elevated temperatures and found that only a slow reaction occurs between ClO and CH_4 and ClO and H_2, *resp.*, even at 587 °C, which seems to prove that a mechanism involving an attack on the fuel by the chlorine atom is more likely than the reaction involving the ClO radical.

Ignition of fuels with perchloric acid

Pearson *et al.* [52—55] have carried out detailed ignition experiments with $HClO_4$ and various fuels in order to clarify the controlling mechanism in the ignition of composite propellants. In the first experiments various polymers were used as fuels [52]. The ignition of fuels by diluted perchloric acid took place much faster and at much lower temperatures (200° to 300 °C) than in the presence of 100% oxygen, when a temperature of about 400 °C was required for ignition. It was, however, not possible to decide whether the important exothermic reactions leading to ignition

Table IX

Ignition delays of polyisobutene (PIB), polyurethane (PU), polystyrene (PS) and polymethylmethacrylate (PMM) mixed with oxygen and perchloric acid vapour [52]

Fuel	Oxidizer	Ignition delay	Temperature, °C	
			Oxidizer	Fuel
PIB	Oxygen	<1 s	441	430
		60 s	357	347
	O_2/Ar (15:10)	<1 s	407	426
		29 s	407	407
		3 min 19 s	351	334
	Perchloric acid (72%)	<1 s	288	272
		23.5 s	258	208
		19 s	179	200
		no ign.	212	20
PU	Oxygen	23 s	429	417
		>3 min, no ign.	353	345
	O_2/Ar (15:10)	60 s	448	455
		94 s	424	441
		>5 min, no ign.	343	317
	Perchloric acid (72%)	<1 s	251	211
		4 s	179	213
		<1 s	295	18
		9 s	295	18
		4.5 s	214	20
		25 s	195	19
PS	Oxygen	50 s	442	457
		>4 min, no ign.	357	343
	O_2/Ar (15:10)	>5 min, no ign.	455	447
	Perchloric acid (72%)	38 s	300	270
		24.5 s	249	220
		158 s	255	224
		>5 min, no ign.	258	215
PMM	Oxygen	>3 min, no ign.	442	445
	Perchloric acid (72%)	2.2 s	303	270
		7 s	245	217
		10 s	304	18
		20 s	237	19

took place between the perchloric acid vapour and the condensed or the vaporized fuel. Some selected results are shown in Table IX.

In order to distinguish between a purely heterogeneous and a purely homogeneous mechanism, the ignition of less volatile solid fuels (nylon, terylene and activated charcoal) and of various gaseous fuels (ammonia, methane, ethylene and isobutene) with 72% $HClO_4$ has been investigated [53].

In the first group of fuels ignition was easily achieved. In the case of gaseous fuels ignition occurred only in the presence of a solid surface. The order of ignitability was ammonia > isobutene > ethylene > methane. Cupric chromate and ferric oxide were very effective catalysts but titanium dioxide, silica and alumina did not produce a detectable reduction in the ignition delay. The behaviour of these catalysts is in accord with their effect on the ignition of ammonium perchlorate. Further experiments indicated that the oxides can promote the ignition of solid fuels, too. *Fuels which are ignited only with difficulty by perchloric acid vapour at 200—250 °C* ignite readily in the presence of catalysts. The catalysts can also lower the temperature of ignition of solid fuels with oxygen but it occurred always at higher temperatures than with perchloric acid [54]. The ignition delay of methyl pentone polymer with perchloric acid vapour in the presence of different added oxides is shown in Table X.

Table X

Ignition delay of TPX (methyl pentone polymer) mixed with perchloric acid vapour in the presence of metal oxides [55]

Catalyst	Ignition delay, s	Temperature °C		Remarks*
		Acid	Fuel	
None	> 300, no ign.	230	224	av. of 6
Alumina Al_2O_3	> 300, no ign.	229	225	
Silica SiO_2	> 300, no ign.	231	226	
Titanium dioxide TiO_2	> 300, no ign.	226	219	
Ferric oxide Fe_2O_3	> 300, no ign.	228	222	av. of 3
Vanadium pentoxide V_2O_5	> 300, no ign.	232	229	
Chromium trioxide CrO_3	> 300, no ign.	233	231	
Chromic oxide Cr_2O_3	> 300, no ign.	237	232	
Tungstic oxide WO_3	> 300, no ign.	240	232	
Zirconium dioxide ZrO_2	> 300, no ign.	221	232	
Molybdenum trioxide MoO_3	> 300, no ign.	230	230	
Magnesium oxide MgO	155.8	235	236	one test > 300
Uranium oxide U_3O_8	58.5	231	225	av. of 2
Cadmium oxide CdO	55.9	236	231	av. of 3
Nickel oxide ($NiO + Ni_2O_3$)	47.6	232	225	av. of 2
Zinc oxide ZnO	34.5	236	231	av. of 2
Cobalt oxide ($Co_3O_4 + Co_2O_3$)	28.1	231	223	av. of 2
Iron oxide Fe_3O_4	16.7	232	224	av. of 2
Manganese dioxide MnO_2	15.2	234	230	av. of 2
Cupric oxide CuO	3.2	232	224	av. of 2
Cuprous oxide Cu_2O	1.8	231	226	av. of 2
Copper chromate	8.1	229	226	av. of 7
Copper chromate (propellant)	7.8	233	228	av. of 5
Copper chromite	1.5	232	228	av. of 6

* av. of 6, etc.: average of six (three, two, etc.) experiments.

An interesting observation is that for ignition to occur the catalyst had to be in physical contact with the fuel [55]. It was postulated that the catalysts act by accelerating the decomposition of perchloric acid, which results in the formation of reactive short-lived intermediates. These could attack the fuel if close enough.

If we compare the relative effectiveness of various catalysts in the above ignition processes with their catalytic effects, on the thermal decomposition of perchloric acid vapour, no direct correlation appears. For instances, in the presence of chromium oxide, which is one of the most effective substance in the decomposition of perchloric acid, ignition did not occur; in contrast, cadmium oxide, which is inactive for perchloric acid decomposition, proved to be quite effective and its efficiency was comparable with that of nickel oxide. This discrepancy indicates that the role of the oxides in the ignition of fuels is not only the acceleration of the decomposition of $HClO_4$ and the production of reactive radicals, but they also promote the oxidation of the fuels. The same is probably valid for the ignition of the ammonium perchlorate propellant when a catalyst is present.

Interaction of $HClO_4$ with ammonium perchlorate

In order to evaluate the decomposition mechanism of ammonium perchlorate (AP) it is very important to know the influence of perchloric acid on the various stages of decomposition of AP. The experimental technique developed for the study of the catalytic decomposition of perchloric acid made it possible to investigate the decomposition of AP in the stream of perchloric acid vapour [56, 57]. It was found that in the presence of the latter, the time lag in the decomposition of orthorhombic AP was significantly reduced and the rate constants of the acceleration period were appreciably higher. The value of the activation energy, however, was almost the same: 30 to 31 kcal/mole both in nitrogen and in nitrogen containing perchloric acid vapour.

Perchloric acid had a similar influence on the decomposition of cubic AP. The activation energy obtained in the presence of perchloric acid was 3 to 5 kcal/mole lower than without it. A study of the effect of the perchloric acid concentration indicated that even $5 \cdot 10^{-8}$ mole of perchloric acid per minute had a markedly promoting effect on decomposition (Fig. 14).

In order to establish more clearly the phase in the decomposition of AP which is influenced by perchloric acid, its introduction into the carrier gas was stopped at different stages of the decomposition process. The results obtained at 220 °C are shown in Fig. 15.

It appeared that for the accelerating effect of perchloric acid to be observed, treatment of the AP sample with perchloric acid for 5 min is sufficient; the course of decomposition subsequently remained practically unaltered, as if perchloric acid were still present during the decomposition.

This may indicate that perchloric acid affects primarily the processes occurring during the time-lag of the decomposition.

In agreement with this, if perchloric acid was introduced onto the AP sample at the very end of the time-lag or during the acceleration period, only a very slight accelerating effect, if any, was experienced.

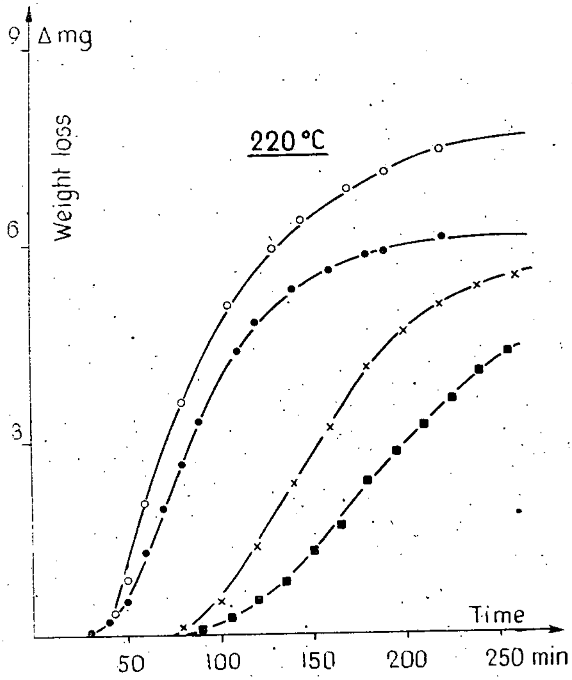


Fig. 14. Thermal decomposition of orthorhombic AP in flowing N_2 containing various amounts of $HClO_4$ vapor [57]. The number of $HClO_4$ moles passed per minute was: $5 \cdot 10^{-7}$ (X); $3.2 \cdot 10^{-5}$ (●); $4 \cdot 10^{-4}$ (○); in pure N_2 (■). The amount of AP was 30 mg.

Microscopic measurements with single crystals indeed revealed that the formation of nuclei was greatly enhanced by the presence of perchloric acid vapour and possibly this resulted in an increased rate of decompositon.

A surprising result was that the extent of decomposition of AP was hardly influenced by the presence of perchloric acid and decomposition stopped at about 25—28% conversion. On the other hand, however, using large amounts (2 g) of the residue of decomposition of AP it was observed, that $HClO_4$ decomposed heterogeneously on the surface of the AP residue. The extent of $HClO_4$ decomposition was 3.8—4.3% at 260 °C and 1.8—2.3% at 240 °C. (The surface area of the AP residue was 1.8 m^2/g, the amount of $HClO_4$ vapour passed was $4 \cdot 10^{-4}$ mole/min, the flow rate of N_2 carrier gas was 95 ml/min). This observation, which was the first experimental proof of the decomposition of $HClO_4$ on the surface of AP, is very important in the elucidation of the decomposition mechanism of the latter. On the basis of this finding it was proposed that the reactive products (chlorine or chlorine oxides) of the decomposition of $HClO_4$ are responsible for the accelerating effect of $HClO_4$ on the decomposition of AP.

Further experiments showed that $HClO_4$ vapour promoted the catalytic decomposition of AP, too. Some results are collected in Table XI.

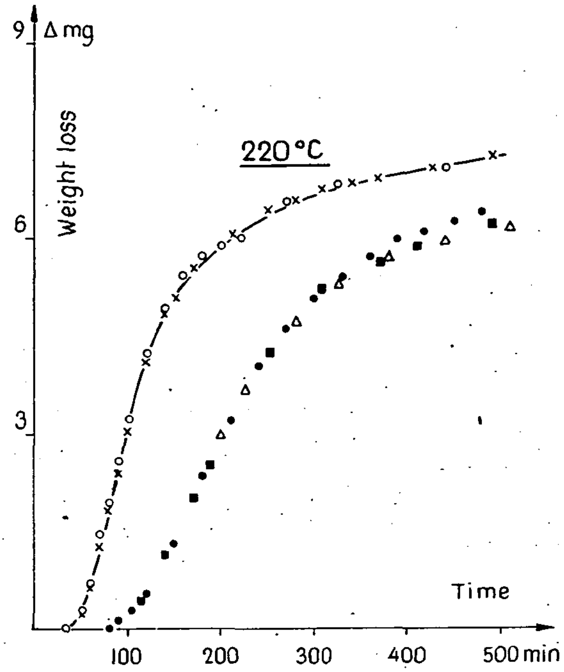


Fig. 15. Thermal decomposition of AP as a function of duration of $HClO_4$ treatment [57]. $HClO_4$ introduction was stopped at 5 min (X) and 30 min (O). Introduction of $HClO_4$: at 105 min (■) and at 195 min (△). Measurement in pure N_2 (●). The amount of AP was 30 mg.

Table XI

The effect of perchloric acid vapour on the catalytic ignition of ammonium perchlorate

Composition Mole ratio; 10:1	Temperature °C	Induction period before ignition (s)	
		without $HClO_4$ treatment	with $HClO_4$ treatment
NH_4ClO_4+ZnO	247	1558	1050
	247	1690	1074
	270	563	299
	270	568	202
	270	—	297
	270	—	206
NH_4ClO_4+CuO	247	no ignition	220
			216
	265	no ignition	—
	270	316	109
	270	320	91
	270	—	105
	270	—	109

The reason for this effect might be sought in a larger part of the $HClO_4$ vapour decomposing on CuO, and thus in a much higher concentration of the reactive species attacking the AP surface.

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ТЕРМИЧЕСКАЯ УСТОЙЧИВОСТЬ ПЕРХЛОРНОЙ КИСЛОТЫ

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Рассмотрены работы занимающиеся вопросами гомогенного термического распада перхлорной кислоты и дан критический обзор представлений о механизме распада.