EFFECT OF COMPOSITE PROPELLANT CATALYSTS ON THE STABILITIES OF HClO$_4$ AND THE HClO$_4$–NH$_3$ SYSTEM

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The vapor-phase decomposition of perchloric acid has been investigated on the components of a composite propellant catalyst—cupric chromite, cupric chromate, and cupric oxide—and also on a Harshaw Cu–0202 catalyst. Cupric chromite, the most effective compound, catalyzed the decomposition of perchloric acid at temperatures as low as 120°C. Cupric oxide had a catalytic effect above 270°C, while cupric chromate decomposed perchloric acid only above 330°C. The interaction between the catalysts and perchloric acid was studied by infrared, kinetic, gravimetric, electric conductivity, chemical and thermal analytical methods. Different types of interaction were found which are strongly temperature-dependent. Infrared spectroscopy showed the formation of a surface perchlorate ion on all the catalysts; the reactivity of this ion presumably plays a decisive role in determining the activity of the catalyst. Parallel to the formation of the surface perchlorate, oxidation of catalysts containing chromite was also observed. The extent of this oxidation became larger at higher temperatures when the decomposition of surface perchlorate occurred. The decomposition of perchloric acid was first order except on chromate, where a zero-order reaction was found. The values of activation energy ranged from 17 to 42 kcal/mole. The high activity of cupric chromite is explained by the high instability of chromium perchlorate.

The effectiveness of the catalysts for the reaction between perchloric acid and ammonia was also investigated. Measurements were made to evaluate the rate of oxidation and reduction of the catalysts with perchloric acid and ammonia at different temperatures.

Introduction

It is known that the combustion processes and the burning rate of composite propellants based on ammonium perchlorate (AP) can be markedly influenced by the presence of small amounts of catalysts. Many attempts have been made to ascertain the detailed mechanism by which such catalysts are effective, through experiments with model mixtures. One of the most promising ways of elucidating the role of the catalyst in this very complex system is to study separately the effect of the catalysts on the individual reactions which most probably occur during the combustion of the propellant.

In the last 10 years, AP catalyst systems have been the subject of especially detailed studies, but no definite conclusion has been reached. It appeared, therefore, that further refinement of such studies was required to evaluate the action of the catalyst in the pyrolysis of perchloric acid vapor and in the reaction of perchloric acid with ammonia. As a first step in this direction, we recently completed a detailed kinetic study on the decomposition of perchloric acid on Cr$_2$O$_3$,[1,2] ZnO,[3] SnO$_2$,[4] and other single oxides,[5] whose effect on the decomposition and combustion of AP had been examined previously.

Based on this study, investigations are now extended to the effect of composite-propellant catalysts. Two basic types of these catalysts can be distinguished: One consists of cupric chromite and the other of cupric chromate; both types contain significant amounts of free cupric oxide.[6] Since the individual processes can be accelerated to different extents depending on the chemical composition of the catalysts, a knowledge of the effect of the components of the composite-propellant catalysts is of fundamental importance in determining the mechanism of their action. The present paper describes studies carried out with the Harshaw propellant catalyst and with its components: cupric chromite, cupric oxide, and cupric chromate.

The primary objectives were to: (i) Establish the relative effectiveness of the components of propellant catalysts, (ii) Ascertain the kinetics and mechanism of the decomposition of perchloric

acid on these catalysts, and (iii) Evaluate the effects of the catalysts on the reaction between perchloric acid and ammonia in the gas phase. In addition, great attention was paid to the interaction of the catalysts and perchloric acid at lower temperatures, as well as at the temperatures prevailing in the composite propellant during the combustion processes.

Experimental

Materials

A.R. perchloric acid was used; it was concentrated to azeotropic composition (73.6%) by passing nitrogen through it at 100°C. The AP was reagent grade material from BDH. Cupric chromite was prepared by thermal decomposition of a 1:1 molar mixture of the nitrates; the product was pressed into pellets, which were sintered at 700°C in air. Cupric and chromium oxides were prepared in a similar way. Cupric chromate was prepared by reacting cupric nitrate with potassium chromate. The precipitate was carefully washed with hot water, and dried at 280°C. The composition of the substances was checked by chemical analysis; it approached the formula composition within 2%.

Methods of Measurement

The decomposition of perchloric acid was studied in a flow system, using nitrogen as carrier gas.[2-4] Approximately 0.2 g catalyst was used in pellet form. The amount of perchloric acid passed in most cases was $2.5-3.0 \times 10^{-5}$ mole/min. The residence time of the perchloric acid in the reaction zone was 0.28 sec. In the kinetic studies, this time was varied between 0.8 and 0.11 sec by changing the flow rate of nitrogen. The adsorption of perchloric acid was followed with a thermo-balance, using a sensitive silica spring incorporated in the catalytic reactor. The same apparatus was used to study the oxidation and reduction of the catalysts. The AP was decomposed slowly in a conventional vacuum apparatus. Its ignition was studied in air at atmospheric pressure. The catalytic gas-phase decomposition of AP was also studied in a vacuum.[3] The burning rate of AP was determined in a Crawford-type bomb at different nitrogen pressures.

Electric conductivity measurements, in the presence of perchloric acid, were made in the catalytic reactor, which was slightly enlarged for this purpose. Infrared spectroscopic analyses were performed with a Unicam SP 100 instrument, using KBr. The surface areas of the catalysts (Table I) were determined by the BET method, using nitrogen at the temperature of liquid air.

Results and Discussion

Decomposition of Perchloric Acid

The catalytic decomposition of perchloric acid occurred at the lowest temperatures on cupric chromite. The decomposition was observed even at 120°C. The catalytic reaction proceeded according to

$$2 \, HClO_4 = Cl_2 + H_2O + 3.5 \, O_2. \tag{1}$$
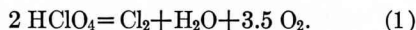
During the conditioning period, 5%–10% hydrogen chloride was also found, but decreased as a function of time. Below 160°C, a few per cent of ClO_2 was detected in the decomposition products. The change of the activity of cupric chromite is shown in Fig. 1. This activity varied only slightly below 145°C, but decreased considerably above 180°C. Under the action of perchloric acid, the color of the catalyst changed from black to brown, indicating its oxidation.

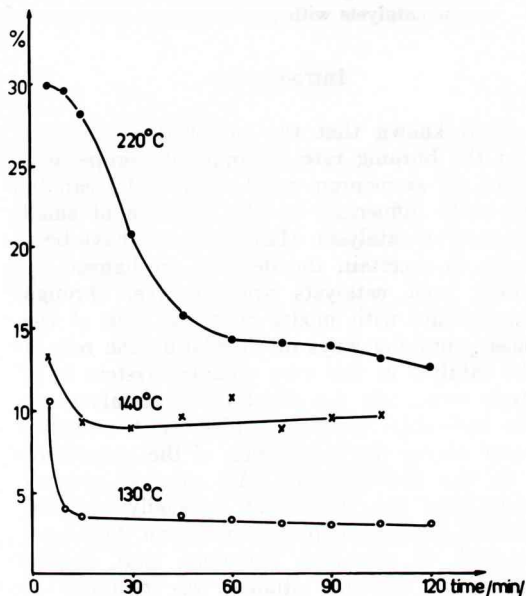The catalytic decomposition of perchloric

FIG. 1. Change in the activity of cupric chromite in the decomposition of perchloric acid. The points indicate the percentage decomposition of perchloric acid at different stages of pretreatment.
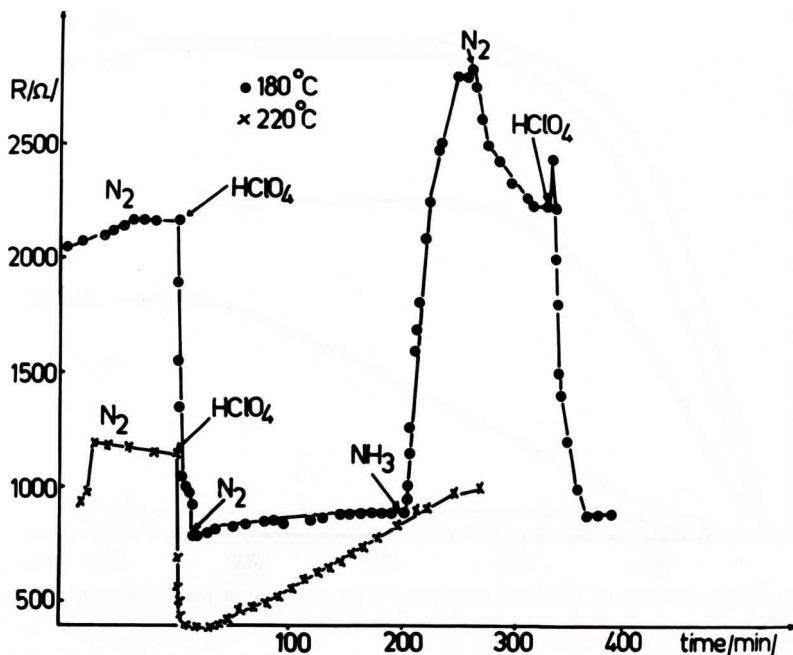
FIG. 2. The electric resistivity of cupric chromite in the presence of perchloric acid and ammonia.

acid on cupric oxide took place at a well-defined rate at 280°–310°C. The reaction products contained O_2, H_2O, Cl_2, and HCl, but no ClO_2 could be detected, which is not surprising since, at these high temperatures, any ClO_2 formed would presumably have decomposed immediately. From the Cl_2 and HCl analyses, up to 85%–90% of the perchloric acid decomposed in Reaction (1), while the remainder reacted according to

$$HClO_4 = HCl + 4\ O_2. \qquad (2)$$
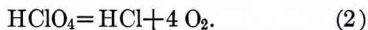
The activity of the cupric oxide decreased initially, but after 30–40 min it had scarcely changed.

The decomposition of perchloric acid on the Harshaw catalyst was observed above 180°C. The reaction products were Cl_2, O_2, and H_2O [Eq. (1)]. During the conditioning period, HCl was also formed. At higher temperatures, the activity of the catalyst suddenly decreased, constant activity being reached only after a fairly long conditioning period.

Cupric chromate proved to be a considerably poorer catalyst for the decomposition of perchloric acid than the other substances tried. 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 Eq. (1).

Interaction of the Catalyst and Perchloric Acid

To permit continuous observation of the interaction between the catalysts and the perchloric acid, a sensitive microbalance was installed in the catalytic reactor. This made it possible to follow the weight change of the catalysts during the catalytic process. When required, the conversion of perchloric acid could be determined simultaneously. To learn more about the nature of the catalyst–perchloric acid interaction, electric conductivity measurements were carried out under the same conditions, and infrared, thermal, and chemical analyses were made of samples treated with perchloric acid at different temperatures. In another series of experiments, the catalysts were treated with perchloric acid at low temperature and heated in nitrogen at 200°–450°C. The resulting changes in the infrared spectra were recorded, and the products of the surface reaction were analyzed.

This study revealed different types of interaction, which are strongly temperature-dependent. In the case of cupric chromite, a significant weight increase (~5%) occurred at the lowest temperature used (120°C). This weight increase became larger with time, and with temperature up to 150°C. Reversible physical
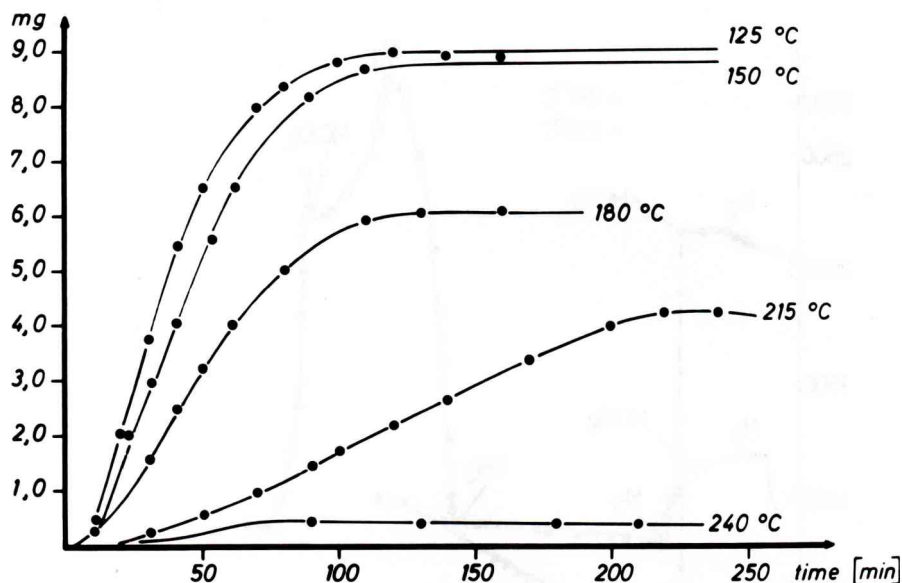
FIG. 3. The weight increase of Harshaw catalysts in the presence of perchloric acid. The amount of catalyst was 30 mg.

adsorption was observed only below 140°C; its contribution to the weight increase never exceeded 10%. Below 140°C, the weight increase was caused largely by the dissociative 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 rapid that even its transitory presence was not detectable by infrared analysis. However, a larger band, belonging to the CrO_4^- anion, appeared on the infrared spectra. Chemical analysis of the catalysts also indicated that, above this temperature, surface oxidation of the catalyst became significant and increased with increasing temperature.

Below 160°C, the electric conductivity of cupric chromite increased only slightly in the presence of nitrogen gas containing perchloric acid; the increase was about half an order of magnitude a⁺ 180°C, and somewhat greater at 220°C. The change in the electric conductivity took place within a few minutes, indicating a very fast interaction, after which the conductivity of the sample slowly decreased. The change of the conductivity proved to be irreversible, the value of conductivity remaining essentially the same when the nitrogen gas containing perchloric acid was replaced with pure nitrogen (Fig. 2). The phenomena observed can be attributed to acceptor-type chemisorption of the perchloric acid and surface oxidation of the catalyst, and hence to an increase of the

excess oxygen content of the electron-hole conducting (p-type) cupric chromite. In accordance with this picture, the electric conductivity of n-type semiconducting oxides decreased considerably in the presence of perchloric acid.[7] The slow decrease in the conductivity, following its initial rapid increase, presumably results from the formation of a surface layer of cupric chromate, which is a poor conductor.

In the case of cupric oxide, the larger part of the perchloric acid adsorbed at 130°–230°C is irreversibly bonded to the oxide. Surface perchlorate ion can be easily detected in this temperature range by infrared spectroscopy. Gravimetric and infrared spectroscopic measurements indicated that the surface perchlorate, formed below 200°C, decomposed at 235°C.

The behavior of the Harshaw catalyst combined the characteristics of both cupric chromite and oxide. Figure 3 shows the weight increase of the catalyst in the presence of perchloric acid at different temperatures. The oxidation of its chromite content was detected as low as 140°C. The formation of surface perchlorate ion was established from 130°–235°C.

In contrast to the previous catalysts, cupric chromate adsorbed perchloric acid even above 300°C, and the bonded perchloric acid decomposed only above 340°C. This indicates a high stabilization of adsorbed perchloric acid due to chromate ion, and agrees with the previous finding that the decomposition of perchloric acid on cupric chromate is negligible below 300°C.

In spite of a large amount of perchloric acid, the electric conductivity of cupric chromate changes very little.

Kinetic Investigations.

In view of the large irreversible effect of perchloric acid on the catalyst surface, kinetic data were obtained at the lowest possible temperatures and conversions (1%–10%), where the oxidative effect of perchloric acid was small.

The decomposition of perchloric acid followed first-order kinetics on cupric chromite at 115°–150°C, when the catalyst was pretreated with perchloric acid to constant activity. The activation energy was 17 kcal/mole. Taking into account that the surface oxidation of cupric chromite is significant, especially at higher temperatures, and that this may influence the kinetic data obtained, 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, a fresh catalyst was used at each temperature, making three measurements which lasted 15 min. In this way, a value of 26 kcal/mole was obtained for the activation energy.

First-order kinetics was found to be valid in the case of cupric oxide at 270°–300°C. The activation energy was 42.8 kcal/mole.

The kinetics of the decomposition of perchloric acid on Harshaw catalyst was investigated in the temperature range of 200°–240°C. The reaction was first-order at all temperatures studied. The rate constants were determined on the catalyst which showed constant activity (~60 min pretreatment). The activation energy was 28 kcal/mole. No change in this value was found when it was calculated from the temperature dependence of the initial rate, using fresh catalyst at every 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 activation energy was 32 kcal/mole.

To sum up the results of the kinetic investigations, it can be stated that cupric chromite is the most active of the solid components of the composite propellant catalysts. Cupric oxide is much less effective, and cupric chromate possesses only a slight activity. (It should be noted that this order of activity is based on the temperature values at which a measurable decomposition of perchloric acid was found.) The loss of activity by cupric chromite can be attributed to its oxidation, and to the formation of the much less active chromate. This conclusion is in disagreement with the assumption of Gilbert and Jacobs.[8] These authors recently studied the decomposition of perchloric acid on different Harshaw catalysts, but the effect of pure cupric chromite, chromate, and oxide was not evaluated. In the case of Harshaw Cu–0203 catalyst, they observed that 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 cupric chromate, formed during the conditioning period, functioned as the actual catalyst. Based on the results of the present investigations of the *individual* properties of the components of Harshaw catalyst, as well as its high cupric oxide content (~80%), it seems more likely that cupric oxide, and not cupric chromate, served as the catalyst at the above temperature. One cannot, however, exclude the possibility that the partially oxidized chromite 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 highly reactive chromite proceeded to a certain extent.

In our earlier investigations,[1–5] it was assumed that the catalytic decomposition of perchloric acid on oxide catalysts involves the formation and decomposition of surface perchlorate ion. On comparing the catalytic activities of oxides with the thermal stabilities of the relevant perchlorates, it appeared that the most active catalysts formed the most unstable perchlorate salts. From this it was concluded that the activity of a catalyst is primarily determined by the stability of the corresponding perchlorate. This may be the reason for the great difference in the catalytic efficiencies of cupric and chromium oxides. Cupric perchlorate decomposes at a measurable rate between 250°–290°C, while chromium perchlorate does so at much lower temperatures of 135°–160°C. Very likely, the decomposition of perchloric acid on cupric chromite occurs in a similar way. The high activity of cupric chromite indicates that it is the chromium (III) ions which determine its effect.

The Effect of Catalysts on the Stability of AP and NH₃–HClO₄

The Effect of Catalysts on the Stability of AP and NH_3–$HClO_4$

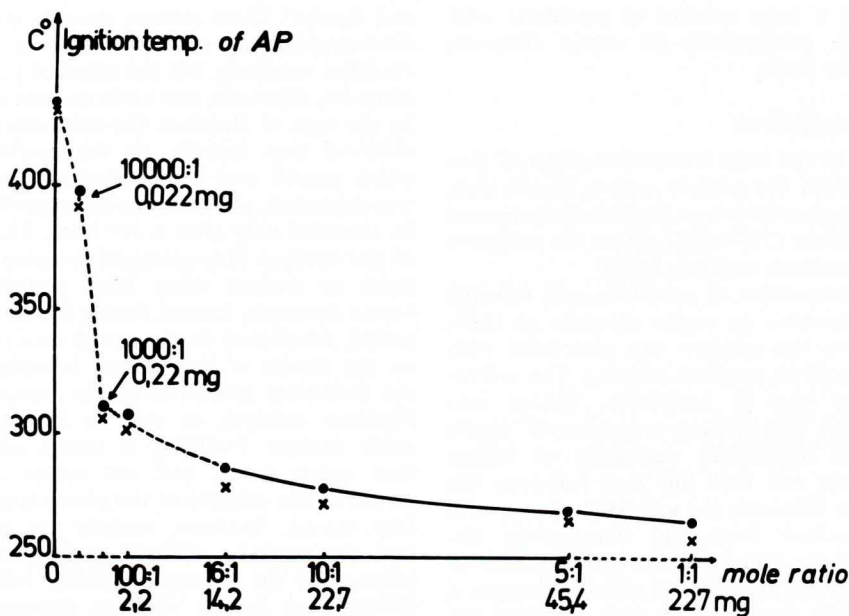Finally, some measurements were made to study the effect of catalysts on the decomposition,

FIG. 4. The minimum ignition temperature of AP as a function of AP:CuCr$_2$O$_4$ mole ratio, and that of CuCr$_2$O$_4$ amount.

ignition, and burning rates of AP, and also on the reactions occurring between perchloric acid and ammonia. It appeared that, up to now, neither the effect of pure cupric chromite nor of the pure chromate alone on these processes had been investigated. The catalysts showed no significant difference in the acceleration of slow decomposition of AP at 240°–260°C. The activation energy was 43 and 41 kcal/mole, respectively, for chromite-catalyzed and chromate-catalyzed decomposition of AP.

It appeared from our earlier studies that both cupric oxide and chromium oxide are extremely effective in bringing about the ignition of AP, decreasing its ignition temperature by almost 180°C.[9,10] Figure 4 shows cupric chromite to be a very effective substance, too. On comparing the effect of different catalysts, it appears that they exert practically the same influence on the ignition process (Table I). The AP exploded at the highest temperature, in the presence of cupric chromate. The activation energies calculated from the temperature dependence of ignition delay range from 22 to 37 kcal/mole.

The burning rate of AP in the presence of these catalysts has been measured up to 100 atm. Although the pressure dependence of burning rates is somewhat different, the following order for the efficiency of additives was established:

$$CuCr_2O_4 > Cu_2Cr_2O_4 > CuCrO_4 > CuO > Cr_2O_3.$$

We also investigated the influence of the above catalysts on the gas-phase decomposition of AP, i.e., on the reaction between HClO$_4$ and NH$_3$ at 300°–400°C. Some results obtained at 320°C are shown in Fig. 5. Electric conductivity measurements, carried out during the reaction, indicate that AP vapors exert practically the same oxidizing effect on the catalysts containing cupric chromite as perchloric acid alone. In other

TABLE I

Surface area of the catalysts, and the lowest ignition temperature of AP in the presence of different catalysts*

Catalyst	Surface area, m²/g	Ignition temp., °C
CuO	1.64	275.8
Cu$_2$Cr$_2$O$_4$	2.24	281.0
CuCr$_2$O$_4$	7.5	273.0
CuCrO$_4$	21.12	284.0
Harshaw Cu–0202	23.25	275.5
Cr$_2$O$_3$	30.61	276.0
Pure AP	—	435.0

* The amount of AP was 100 mg; AP:catalyst mole ratios were 10:1.
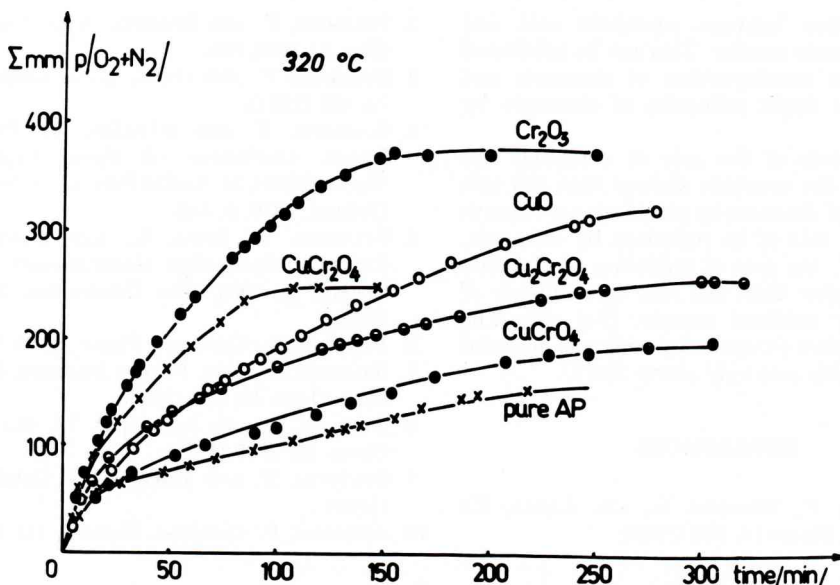
FIG. 5. The effect of additives on the gas-phase decomposition of AP at 320°C.

words, the reducing effect of ammonia cannot be noticed, probably because of the high excess of oxygen in the system.

The effect of cupric chromite at the beginning always exceeded that of cupric oxide (Fig. 5). It is interesting that cupric chromate had little effect. This behavior is no doubt connected with the relatively small effect of the cupric chromate on the decomposition of perchloric acid at this temperature. This may be due to the fact that, at 320°C, cupric chromate hardly catalyzes the oxidation of ammonia by molecular oxygen; in

the present case, this could be explained by the interaction of ammonia and cupric chromate being rather slow at this temperature. Considering the fact that cupric chromate brought about the explosion of AP even at 284°C, it can be concluded that a significant role is played here by the acceleration of the condensed-phase decomposition of AP, in which the slow, rate-determining process differs from that of the gas-phase reaction. At the higher temperatures of 360°–400°C, the difference between the efficiency of chromite and chromate with respect
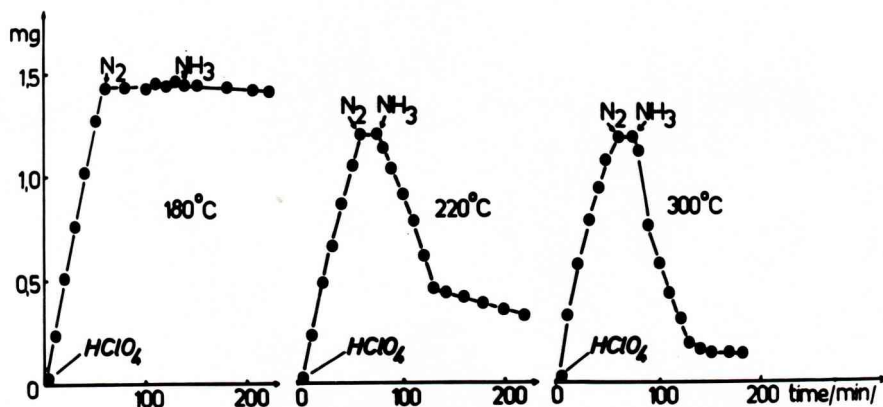

FIG. 6. The oxidation of cupric chromite by perchloric acid, and the reduction of the oxidized sample by ammonia. The ammonia content of the nitrogen carrier gas was practically equal to that of perchloric acid $(2.5 \times 10^{-5}$ mole/min).

to the reaction between perchloric acid and ammonia became smaller. This can be attributed partly to the decomposition of chromate and partly to the faster reduction of chromate by ammonia.

Measurements of the rate of oxidation and reduction of the catalysts showed that the rate of oxidation of chromite by perchloric acid always exceeded the rate of its reduction by ammonia. Below 220°C, the rate of oxidation of chromite was even higher than the rate of reduction of the partially oxidized sample (Fig. 6). The reduction of pure chromate by ammonia occurred at a measurable rate only above 330°C.

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COMMENTS

A. R. Hall, Ministry of Defense, Rocket Propulsion Establishment, Westcott, Aylesbury, Buckinghamshire, U.K. Using opposed jet diffusion flames of ammonia and 72% perchloric acid vapor, we added (to the ammonia) small amounts of a range of volatile metal compounds, including those of Cu, Cr, Mn, and Fe, to see if there was any enhancement of the "flame strength," as indicated by the blowout point. No such catalytic effect occurred. This negative result might be thought to relate only to the particular flame system; particles of solid metal compounds might not be formed at the right place at the right time. However, a different fuel–oxidizer combination did reveal a strong catalytic effect that was also shown in the premixed flame. So the combined results seem to support the view that, in the combustion of AP, catalysts exert their effect in, or on the surface of, the solid phase rather than in the gas phase.