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NOTES

Catalytic Decomposition of $HClO_4$ Vapor over CuO by Field Ion Mass Spectrometry

The study of the catalytic decomposition of perchloric acid is of practical importance since $HClO_4$ is one of the dissociation products of ammonium perchlorate, the most generally used oxidizer in composite propellants. Recent kinetic studies (*1–6*) have revealed the general features of the catalytic decomposition of perchloric acid on oxide surfaces and have shown a correlation between the efficiencies of the oxides and the thermal stabilities of corresponding perchlorate salts (*4*). The chemical analysis of reaction products, however, did not allow the detection of unstable transitory species which supposedly play a dominant role in the catalytic combustion of ammonium perchlorate based propellants.

In principle, mass spectrometric analysis should be applicable for detecting volatile intermediates of this reaction; in practice, however, fragmentation due to electron impact causes a considerable difficulty in evaluating the products.

Recently we have investigated the field ionization of perchloric acid on Pt and W emitters (*7*). Both emitters are stable enough for the field ionization of perchloric acid. On a Pt emitter, conditions were found where the field ionization occurred with an insignificant amount of fragmentation and the intensity of $HClO_4^+$ ions increased linearly with the partial pressure of $HClO_4$. Based on these results this technique has now been used in the analysis of $HClO_4$ decomposition catalyzed by CuO.

Two grams of granulated CuO (Riedel) with a BET surface area of 6.6 $m^2\ g^{-1}$ were used as the catalyst, and the perchloric acid was a constant boiling A. R. grade material containing water to the extent of 72% by weight of $HClO_4$. The decomposition was carried out in a microcatalytic reactor incorporated in a homemade field ion source (Fig. 1) which was part of a CH4 Atlas MAT mass spectrometer [for details, see Ref. (*7*)]. A glass bulb containing perchloric acid was directly connected to the catalytic reactor by a metal leak valve, and a continuous stream of perchloric acid vapor was attained by con-

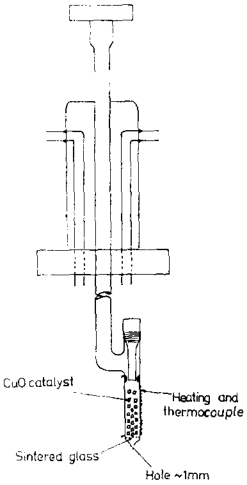

FIG. 1. Microcatalytic reactor which was incorporated in the field ion source. The reactor exit was about 5 mm in front of the field emitter and could be adjusted (by bellows, not shown) to maximum intensity.

TABLE 1

Absolute and Relative Intensities of Products of Catalytic Decomposition of $HClO_4$(72%) on CuO Evaluated by Field Ionization Mass Spectrometry[a]

T_R (°C)	$HClO_4$ (mV)	Cl_2 (mV)	$Cl_2/$ $HClO_4$	ClO (mV)	ClO/ $HClO_4$	ClO_2 (mV)	$ClO_2/$ $HClO_4$	ClO_3 (mV)	$ClO_3/$ $HClO_4$	ClO_4 (mV)	$ClO_4/$ $HClO_4$
25	23	0.02	0.0009	0.11	0.0478	0.12	0.0052	0.39	0.0169	0.06	0.0026
55	20.5	0.01	0.0005	0.08	0.0039	0.07	0.0034	0.38	0.0185	0.11	0.0053
80	22.5	0.01	0.0005	0.15	0.0066	0.11	0.00488	0.5	0.0222	0.2	0.0088
100	20.8	0.01	0.0005	0.16	0.0077	0.265	0.0127	0.49	0.0235	0.35	0.0168
120	19.5	0.05	0.0025	0.26	0.0133	0.88	0.0451	0.46	0.0236	0.24	0.0123
155	12.0	0.2	0.0166	0.3	0.025	1.6	0.1333	0.25	0.0208	—	—
180	9.5	0.23	0.0242	0.295	0.0310	1.65	0.1736	0.18	0.0189	—	—
215	7.8	0.36	0.0461	0.3	0.0384	1.73	0.2218	0.15	0.0192	—	—
260	2.7	0.42	0.1555	0.295	0.1092	2.15	0.7963	—	—	—	—
285	1.35	0.41	0.3037	0.34	0.2518	2.35	2.6296	—	—	—	—

[a] The pressure of $HClO_4$ in the reaction chamber was ~0.1 Torr.

tinuous pumping. The pressure of $HClO_4$ in the reaction chamber was ≈0.1 Torr (1 Torr = 133.3 $N\ m^{-2}$). The perchloric acid and its catalytic decomposition products enter the ionization chamber, which had a Pt emitter ca. 5 mm in front of the reactor exit. The emitter was usually kept at a highly stabilized potential U_0 of +4.5 kV, and the field strength at the emitter surface was regulated by the potential U_1 of the luminescent screen. The potential difference $U = U_0 - U_1$ is proportional to the field strength and ions are emitted with an energy which is determined by U_0.

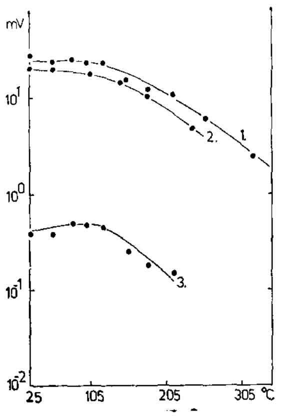

FIG. 2. (1) $HClO_4^+$ current (mV scale proportional to current) as a function of reactor temperature T_R (2) Reproduction of the (1) in a second experiment. (3) ClO_3^+ current as a function of reactor temperature T_R.

The field ionization mass spectral data of the gas outlet at different temperatures are shown in Table 1. Since the ionization probabilities of different molecular species at or near the emitter surface are different, field ion intensities in general will allow only an approximate comparison of neutral concentrations. If the ionization step is merely electron tunneling into the emitter tip, ionization energies [(eV) in parentheses] can be a rough indication of the order of detectability:

$$ClO_2(10.7);\ ClO(11.1);\ ClO_3(11.7);\ HClO_4(13.4);\ O_2(12.06).$$

Accordingly, the chlorine oxides, ClO_2, ClO and ClO_3, should be easily detected on account of the substantially higher ionization probability compared to $HClO_4$.

A plot of the $HClO_4^+$ current vs reactor temperature T_R is shown in Fig. 2. The current was practically constant for T_R between 25 and 120°C and with a tip temperature T_t of 25°C. Some fragment ions appeared even at T_R = 25°C and these are due to a slight instability of the parent molecular ion. The relative intensities (% of the $HClO_4^+$ peak) of chlorine oxide ions, such as ClO, ClO_2, ClO_3, and ClO_4, at this temperature were at a low level (for instance the value for ClO_3^+ was 1.7 and that for ClO_2^+, 0.5) in good agreement with the values obtained previously for the field ionization of $HClO_4$ on Pt emitters under comparable conditions (*7*). This is to be compared with values of 250 and 400, respectively, using electron impact mass spectrometry (70 eV), indicating the large fragmentation probability of $HClO_4^+$ under those conditions.

A decrease in the $HClO_4^+$ ion intensity due to decomposition was observable only above 120°C. The onset of decomposition is indicated more sensitively by the change in the intensity of the ClO_2^+ ion. The ClO_2^+ ion current was doubled even at 100°C and increased markedly with further increase of reaction temperature. At $T_R = 285°C$ the amount of ClO_2^+ exceeds even that of $HClO_4^+$ (Fig. 3).

The intensity of ClO_3^+ decreased when decomposition started; its ratio to $HClO_4^+$ ion was practically constant between 25 and 215°C (Fig. 2), indicating that ClO_3^+ is primarily the product of field fragmentation of $HClO_4^+$ on the Pt emitter and is probably not being formed in catalytic decomposition of $HClO_4$.

A slight increase in the intensity of ClO^+ and Cl_2^+ ions occurred at the threshold decomposition temperature of $HClO_4$ (T_R = 120°C) and it remained constant up to T_R = 285°C. Their intensity relative to $HClO_4^+$ gradually increased with the temperature above T_R = 120°C. The fact that there are no trends of ratios ClO^+/ClO_2^+ and Cl_2^+/ClO_2^+ with temperature indicates that these species are not the products of ionic fragmentation of ClO_2^+.

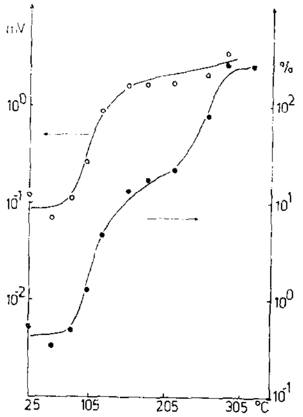

Fig. 3. Absolute (left scale) and relative intensities of ClO_2^+ as a function of reactor temperature T_R.

Some independent measurements have also been carried out with this CuO catalyst in the flow reactor used previously for the catalytic decomposition of $HClO_4$ (*1–6*). The flow rate of carrier gas (N_2) was ca. 150 ml min^{-1}, and the amount of perchloric acid passed per minute was 3×10^{-5} mol. Measurable decomposition in this reactor was first detected at 220°C. Chemical analysis indicated only the formation of chlorine, oxygen and water, the reaction following first order kinetics with an activation energy of 160.73 kJ mol^{-1}.

The product distribution of the CuO-catalyzed decomposition of $HClO_4$ observed by field ionization over a Pt emitter differs basically from that of the homogeneous decomposition of $HClO_4$, that of the fragmentation due to electron impact (*8*, *9*) or that of the field ionization on a W emitter (*7*). In all these cases the main product is the ClO_3 radical or ion which is formed in the primary step of $HClO_4$ decomposition

$$HO\text{-}ClO_3 = OH + ClO_3,$$

or

$$HClO_4^+ = OH + ClO_3^+.$$

These steps are probably less important in the decomposition of $HClO_4$ catalyzed by CuO. The present results support the suggestion that the first step in the catalytic decomposition over CuO is the dissociative chemisorption of $HClO_4$ on the oxide surface

$$HClO_{4(g)} = H_{(ads)}^+ + ClO_{4(ads)} .$$

This is followed by bimolecular decomposition of surface perchlorate ions and the formation of water

$$2\,H_{(ads)}^{+} + 2\,ClO_{4(ads)}^{-} = H_2O_{(g)} + 2\,ClO_2 + \tfrac{3}{2}O_2.$$

In a minor step, the decomposition of surface ClO_4^- ion yields ClO and Cl_2.

The appearance of ClO_4^+ ion in field ion mass spectra may also be discussed in terms of the dissociative adsorption of $HClO_4$. The intensity of ClO_4^+ ions is very low but under decomposition conditions is definitely higher than in field fragmentation. The intensity of ClO_4^+ ions gradually increases with the temperature up to 100°C suggesting the occurrence of activated adsorption of $HClO_4$. At 120°C when the decomposition starts the intensity of ClO_4^+ ions decreases and at higher temperatures it vanishes completely. The key step in the decomposition is very likely the decomposition of the surface perchlorate ion. The maximum of ClO_4^+ may then be explained by the desorption of already excited $HClO_4$ molecules.

The conclusion regarding the decomposing surface perchlorate is supported by the correlation between the catalytic efficiency of oxides and the stability of corresponding perchlorate salts, where it was found that the most active oxides gave the most unstable perchlorates (*4*).

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REFERENCES

1. Solymosi, F., Börcsök, S., and Lázár, E., *Combust. Flame* **12**, 397 (1968).
2. Solymosi, F., and Börcsök, S., *J. Chem. Soc. A* 601 (1970).
3. Solymosi, F., and Gera, L., *J. Phys. Chem.* **75**, 491 (1971).
4. Solymosi, F., Geral. L., and Börcsök, S., *Int Symp. Combust., 13th* (Combust. Inst., Pittsburgh) 1009 (1971).
5. Gilbert, R., and Jacobs, P. W. M., *Can. J. Chem.* **49**, 2827 (1971).
6. Korobeintchew, O. P., Karpenko, Y. Y., and Boldyrev, V. V., *Izv. Akad. Nauk* **7**, 1663 (1970).
7. Solymosi, F., and Block, J. H., *Ber. Bunsenges. Phys. Chem.* **79**, 686 (1975).
8. Heath, G. A., and Majer, J. R., *Trans. Faraday Soc.* **60**, 1783 (1964).
9. Fischer, I. P., *Trans. Faraday Soc.* **63**, 684 (1967).

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