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Chemistry of the Incomplete Decomposition of Ammonium Perchlorate (AP)

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Results are presented to show that as the thermal decomposition of orthorhombic ammonium perchlorate proceeds there is an accumulation, in the solid, of hydrochloric and nitric acids, the concentrations of which increase up to 15% decomposition after which they decrease until they reach the original values.

Introduction

Various investigators have studied the thermal decomposition of ammonium perchlorate (AP) from essentially different viewpoints (*1–4*). It should be recalled that below 250°C orthorhombic AP decomposes in an incomplete fashion, i.e., the decomposition terminates after 30% (*5–7*); the residue remaining behind is physically and chemically AP (*8*). Most chemical studies of the thermal decomposition of AP have been analyses of the gaseous decomposition products of AP (*8–26*) and their effects on the decomposition (*8, 27–33*). However, there have been few studies of the chemical nature of the problem of incomplete decomposition of AP. In fact very few chemical analyses of partially decomposed AP (the residue left behind after decomposition) have been carried out.

Bircumshaw and Newman (*8*), who carried out the first investigation on the kinetics of decomposition of AP, reported that the residue remaining after 30% decomposition of AP at 230°C contains traces of chloride ion and nitrogen tetroxide. Osada and Sakamoto (*34*) found that AP becomes acidic at 220°C, reaches a value of maximum acidity at 240°C, and then decreases in acidity above 250°C. The absence of HCl, HNO_3, and HNO_2, by spot tests, led them to conclude that the acid present is $HClO_4$. Klimenko and Frolov (*35*) also claimed that the $HClO_4$ produced remains in the condensed phase during the initial stages.

Different interpretations based on various physicochemical measurements have been put forward (*1, 36*) to explain the incomplete decomposition of orthorhombic AP. The interpretation which is pertinent to this work and is widely accepted is based on the fact that some of the ammonia (NH_3) liberated from the reaction

$$NH_4^+ + ClO_4^- \overset{kT}{\rightleftharpoons} NH_3 + HClO_4$$

is adsorbed at selective sites. Jacobs and Whitehead (*1*) argue that the NH_3 thus adsorbed subsequently combines with perchloric acid ($HClO_4$) to form AP, before the $HClO_4$ has a chance to decompose, and the reaction thus comes to an end. They have

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presented indirect evidence to confirm this view (*1*).

Recently Boldyrev *et al.* (*36*) presented a slightly modified version of the theory of Jacobs *et al.* (*1*). The

> primary stage of the thermal decomposition of AP is a proton transfer resulting in ammonia and perchloric acid. The subsequent decomposition of perchloric acid and an oxidation of ammonia by products of the acid's decay result in final products of the reaction. ... If the dissociation proceeds at individual and aligned dislocations one should expect an accumulation of perchloric acid and the removal of ammonia in these parts of the crystal, because the removal rate of gaseous molecules from pores is inversely proportional to the square root of the molecular weight of the gas. The acid accumulated in this way in a dislocation can be removed in two ways.

If the decomposition of AP at 230°C is prematurely terminated, say when 10–15% of it has decomposed and the pH ($pH = -\log[H^+]$, where $[H^+]$ is the hydrogen ion concentration) of an aqueous solution of the residue has been measured, the pH should be alkaline according to Jacobs *et al.* (*1*) and it should be acidic according to Boldyrev *et al.* (*36*). This paper presents a direct illustration of how the pH of the isothermally decomposing orthorhombic AP changes with time or extent of the decomposition.

Experimental

The AP used throughout this investigation was of Analar grade from BDH. Experiments were also repeated on the same AP crystallized from double-distilled water and also on AP from Fluka, recrystallized once. The particle size (63–90 μ) and the age of the AP used as the starting material and of the subsequently decomposed AP used for further experimentation were kept constant. The thermal decomposition was followed on a home-made thermogravimetric setup described earlier (*37*). The furnace temperature was kept constant (±1°C). Four different experiments were carried out in the work. (a) pH measurement: 1.20 g of the sample was dissolved in 100 ml of double-distilled water and pH measurements were made on a SYSTRONICS pH meter capable of reading to the second decimal place. (b) Estimation of H^+ by iodometry: 0.1 *M* AP solutions were prepared. A standard solution of potassium iodate and potassium iodide was added to 25 ml of the 0.1 *M* AP solution and the iodine liberated was titrated against a standard solution of 0.01 *M* sodium thiosulfate using a starch indicator. The error in this method was found to be 10% in this concentration range. $[H^+]$ was also calculated directly from the values of pH, and the results obtained from the two methods were found to tally with each other (Table I). (c) Chloride estimation by Volhard's method: 0.1 *M* AP solutions were prepared. To 20 ml of this solution was added 25 ml of 0.01 *M* silver nitrate solution, and the excess of silver nitrate was titrated against 0.01 *M* standard potassium thiocyanate. The error in this estimation was found to be 5% in this concentration range. (d) Spot test for nitrate: The reagent used for the spot test was diphenyl amine (DPA) dissolved in concentrated sulfuric acid. About 100 mg of the DPA was dissolved in 10 ml of the acid. Saturated solutions of AP were prepared in this case. The test is not sensitive if the concentration of DPA in H_2SO_4 is greater.

Results

Figure 1 presents a plot of the hydrogen ion concentration, $[H^+]$ ($pH = -\log[H^+]$; the hydrogen ion concentration was also determined iodometrically), of AP at various stages of decomposition at 230°C versus α, the fraction of the salt decomposed. It can be seen that the H^+ concentration increases systematically, reaching a maximum value when α is about 0.15 (when $\alpha = 0.3$ the reaction stops), after which it decreases to attain the original value and the reaction terminates. It is worth mentioning that a plot of $d\alpha/dt$ versus α is also of the same nature, with the maximum occurring at about $\alpha = 0.15$ (Fig. 2). Also presented in Fig. 1 is the

TABLE I

DATA ON THE ANALYSIS OF AP PARTIALLY DECOMPOSED AT 230°C[a]

Percentage decomposed	$[\mathrm{Cl}^-]$ (moles/liter)	$[\mathrm{H}^+]$ (moles/liter)		Mole% of Cl^- present in AP	Mole% of H^+ present in AP	Estimation of NO_3^-	
		From pH measurements	From iodometry			Percentage decomposed	Concentration of NO_3^-
0.0	0.00000	0.00000	0.00000	0.00000	0.00000	0	Absent
4.3	—	0.00003	0.00003	0.00000	0.03133	12	Present
10.8	0.00060	0.00129	0.00116	0.58956	1.26136	30	Absent
18.3	0.00053	0.00063	0.00063	0.51739	0.61785	—	—
23.3	0.00001	0.00000	0.00000	0.00979	0.00000	—	—
30.0	0.00000	0.00000	0.00000	0.00000	0.00000	—	—

[a] Maximum error allowed: chloride estimation, 5%; acid estimation, 10%.

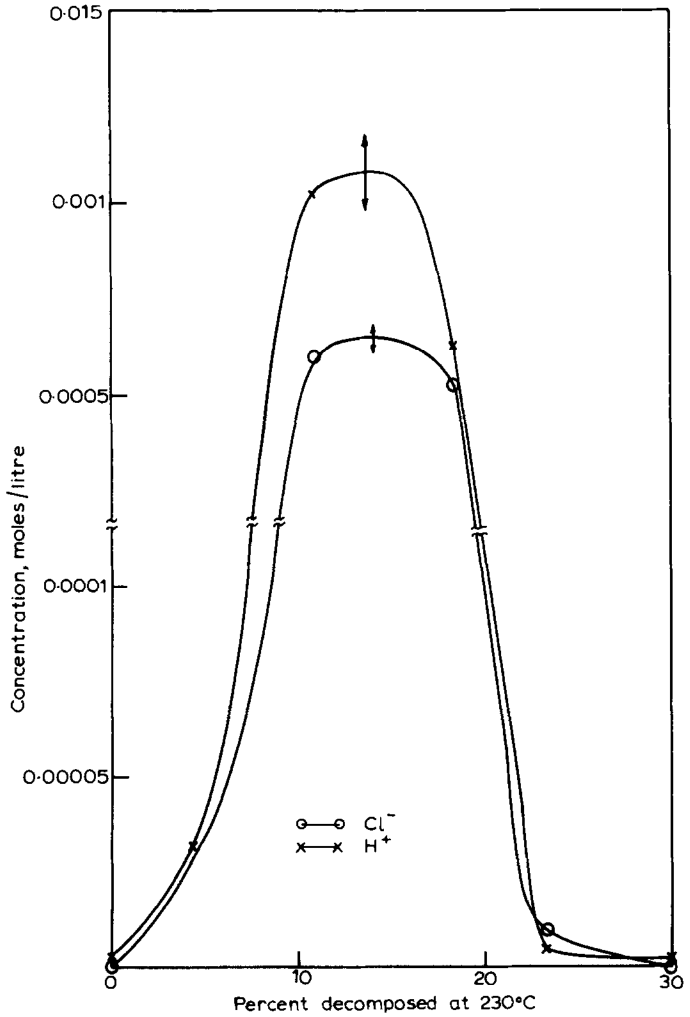

FIG. 1. Plot showing the variation of hydrogen and chloride ion concentrations (moles/liter) with percentage AP decomposed at 230°C.

variation of the chloride ion concentration [Cl^-] with α. This behavior is seen to be identical to that of H^+. A careful analysis, however, reveals that although the orders of magnitude of [H^+] and [Cl^-] are the same, there is quantitatively more [H^+] than [Cl^-], specifically at $\alpha = 0.15$. It was not possible to measure the concentration of nitrate ion (NO_3^-) quantitatively. Spot tests, however, definitely revealed that NO_3^- in the decomposing AP followed the same trend as H^+. Details of the above experiments are summarized in Table I.

A similar analysis of the decomposing AP in the cubic form definitely showed the absence of H^+, Cl^-, NO_3^-, and NH_3.

Discussion

The results presented in the present investigation show beyond doubt that hydrochloric acid and nitric acid accumulate in the decomposing crystal, the extent being roughly 1 mole% of AP concentration at $\alpha = 0.15$ (Table I). HCl and HNO_3 are undoubtedly the decomposition products arising from the oxidation of NH_3 by the decomposition products of $HClO_4$. This suggests that up to $\alpha = 0.15$, $HClO_4$ decomposes preferentially rather than recombining with NH_3, i.e., $HClO_4$ and NH_3 are physically, on a molecular level, separated from each other. As pointed out by Boldyrev *et al.* (*36*), the pores of the wall become larger as a result of the interaction of the products of $HClO_4$ decomposition with unreacted AP on the walls of the pore and $HClO_4$ molecules can now diffuse through the pores as easily as the smaller molecules of NH_3. This results in recombination and the reaction terminates.

When the thermal decomposition of AP is carried out in an atmosphere of NH_3 gas the reaction is known to be drastically desensitized (*1*). The excess of NH_3 molecules makes possible back-diffusion of NH_3 to the center where $HClO_4$ is accumulating, leading to a recombination of NH_3 and $HClO_4$. An atmosphere of $HClO_4$, however, has no effect on the decomposition except during the induction period (*30*). The bulky $HClO_4$ molecules simply cannot back-diffuse into the crystal.

One can, however, argue at this juncture that the increases in the concentrations of H^+, Cl^-, and NO_3^- with decomposition and the subsequent decreases constitute a phenomenon to be expected, as the acid production will naturally be greater in the acceleration stage of the reaction. Then by analogy one would expect a similar trend in the decomposition of cubic AP. But the present investigation derives its importance from the finding that in cubic AP there are no changes in the concentrations of H^+, Cl^-, and NO_3^- and that they do not accumulate in the solid during decomposition as it happens in orthorhombic AP. This, however, does not mean that H^+, Cl^-, and NO_3^- are not produced in the thermal decomposition of cubic AP. The results definitely show that these products are not trapped in or adsorbed onto the AP crystal in cubic form. One can speculate that the pore size of the wall is already large enough in cubic AP to allow the molecules of both $HClO_4$ and NH_3 to diffuse through easily. Bircumshaw and Newman (*8*) and subsequently Maycock and Pai Verneker (*5*) have in fact shown how the phase transition from orthorhombic to cubic at about 240°C affects the rate of thermal decomposition of AP: (i) The rate of decomposition at 260°C is less than that at 230°C; and (ii) whereas orthorhombic AP decomposes in an incomplete fashion, cubic AP decomposition goes to completion. The present data in fact complement the earlier work of Bircumshaw and Newman (*8*) and in addition provide clues as to why AP in orthorhombic form decomposes in an incomplete fashion whereas cubic AP decomposition goes to completion. Finally, one could also speculate that the very mechanisms of decomposition in the two

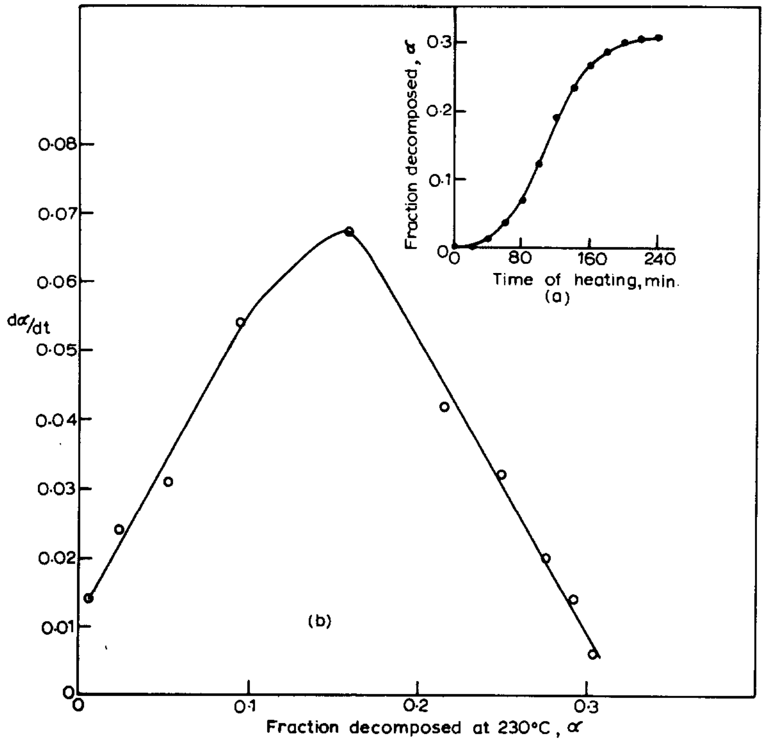

FIG. 2. (a) Plot of α, the fraction of AP decomposed versus t, the time of heating at 230°C. (b) Plot of the rate of decomposition $d\alpha/dt$, obtained from Fig. 2a (dt is equal to 20 min) versus α, the fraction of the AP decomposed at 230°C.

crystal forms of AP are different, i.e., the primary products of decomposition in the two forms are different. This could be supplemented by the respective activation energies of 30 and 20 kcal mole^{-1} and the fact that even the final decomposition products are different in the two different crystal forms of AP.

References

1. P. W. M. JACOBS AND H. M. WHITEHEAD, *Chem. Rev.* **69**, 551 (1969).
2. A. G. KEENAN AND R. F. SIEGMUND, *Quart. Rev.* **23**, 430 (1969).
3. G. S. PEARSON, *Oxid. Combust. Rev.* **4** (1969).
4. A. R. HALL AND G. S. PEARSON, RPE Technical Report No. 67/1, London, West Cott. (January 1967).
5. J. N. MAYCOCK AND V. R. PAI VERNEKER, *Proc. Roy. Soc. Ser. A* **307**, 303 (1968).
6. V. R. PAI VERNEKER AND K. RAJESHWAR, *J. Solid State Chem.* **17**, 27 (1976).
7. V. R. PAI VERNEKER AND K. RAJESHWAR, *Int. J. Phys. Chem. Solids* **37**(1), 63–66 (1976).
8. L. L. BIRCUMSHAW AND B. H. NEWMAN, *Proc. Roy. Soc. Ser. A* **227**, 115 (1954).
9. M. DODE, *Bull. Soc. Chim. Fr.* **5**(5), 170 (1938).
10. M. DODE, *C.R. Acad. Sci. Paris* **200**, 63 (1934).
11. L. L. BIRCUMSHAW AND B. H. NEWMAN, ERDE Report No. 8/EMR/50 (1951).
12. H. M. CASSEL AND I. LIEBMAN, *J. Chem. Phys.* **34**, 342 (1961).
13. W. A. ROSSER, S. H. INAMI, AND H. WISE, *in* "Proceedings, Third ICRPG Combustion Conference, February 1967," Vol. 1, pp. 27–28, CPIA Publication No. 138.
14. G. A. HEATH AND J. R. MAJER, RPE Technical Note No. 219 (April 1963).
15. G. A. HEATH AND J. R. MAJER, *Trans. Faraday Soc.* **60**, 1783 (1964).
16. B. B. GOSHGARIAN AND J. A. WALTON, Technical Documentary Report AFRPL-TR-65-87 (April 1965).

17. J. N. Maycock and V. R. Pai Verneker, *J. Chem. Phys.* **47**, 3618 (1967).
18. P. J. Herley and P. W. Levy, *J. Chem. Phys.* **49**, 1493 (1968).
19. F. Volk and H. Schubert, *Explosivestoffe* **18**, 73 (1970).
20. G. L. Pellett, *AIAA J.* **8**, 1560 (1970).
21. Yu. A. Zakharov, R. N. Isaev, and V. V. Bordachev, *Zh. Fiz. Khim.* **44**, 302 (1970).
22. W. E. Baumgartner, J. A. Hammond, W. G. Stapleton, and Y. A. Tajima, West States Sect. Combust. Inst. (Pap), WSS/Cl-69-19 (1969).
23. G. L. Pellett and A. R. Saunders, *in* "Proceedings, Third ICRPG Combustion Conference, 1967," Vol. I, p. 29, CPIA Publication No. 138.
24. G. L. Pellett and A. R. Saunders, AIAA Sixth Aerospace Science Meeting, AIAA Preprint 68-149 (1968).
25. G. L. Pellett and A. R. Saunders, NASA Tech. Memo, NASA-TM-X-59227 (1966).
26. O. P. Korobeinichev, A. G. Tereshchenko, and G. I. Anisiforov, *Fiz. Goreniya Vzryva* **12**(4), 633–636 (1976).
27. J. V. Davies, P. W. M. Jacobs, and A. Russel-Jones, *Trans. Faraday. Soc.* **63**, 1737 (1967).
28. B. S. Svetlov and V. A. Koroban, *Kinet. Katal.* **8**(2), 456–459 (1967).
29. V. A. Koroban, V. M. Chugunkin, A. N. Kudryavtseva, and B. S. Svetlov, TR. Mosk. Khim-Tekhnol. Inst. No. 76, 50–5 (1970).
30. F. Solymosi, *Acta. Phys.* **19**(1–2), 67–94 (1973).
31. D. Thomas, B. Bregeon, A. Cointot, A. Hardy, and M. L. Bernard, *Progr.-Vac. Microbalance Tech.* **3**, 281–292 (1975).
32. F. Solymosi and S. Borcsok, *Combust. Flame.* **25**, 136 (1975).
33. Yu. I. Rubtsov, L. P. Andrienko, and G. B. Manelis, *Zh. Fiz. Khim.* **51**(1), 70–73 (1977).
34. H. Osada and E. Sakamoto, *Kogyo Kayaku Kyokai-shi* **24**, 236–244 (1963).
35. G. K. Klimenko and E. I. Frolov, *in* "Proceedings, Gorenie Vzryv, Mater. Vses. Symp. 3rd, 1971," pp. 745–747 (1972).
36. V. V. Boldyrev, Yu. P. Savintsev, and T. V. Moolina, *in* "Proceedings, Seventh International Symposium on the Reactivity of Solids, Bristol, July 1972," pp. 17–21.
37. J. W. McBain and A. M. Baer, *J. Amer. Chem. Soc.* **48**, 600 (1926).