The Catalytic Decomposition of Potassium Perchlorate

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Received June 28, 1979

The thermal decomposition of potassium perchlorate in the presence of various metal oxides was investigated by thermogravimetry and by isothermal weight loss techniques. The effect of metal oxide concentration on the temperature of initial deflection, T_i, of thermogravimetry curves of metal oxide/ potassium perchlorate mixtures was determined. The Arrhenius parameters were also tabulated to demonstrate the effect of metal oxide concentration on the rate of decomposition of the potassium perchlorate.

Introduction

The catalytic effect of metal oxides on the thermal decomposition of chlorate and perchlorate salts has been the subject of several investigations. Early studies which relate to the catalytic decomposition of chlorates include a three part series by Brown *et al.* [1–3] utilizing MnO_2 and Fe_2O_3 catalysts, an investigation by Otto and Fry [4] to delineate the role of potassium chloride in the decomposition process, and an analysis of the influence of Fe_2O_3 impurities in MnO_2 on the catalytic process [5]. Perchlorate decomposition, including kinetic data on the ferric oxide catalyzed reaction, was reported in a 1923 study by Otto and Fry [6], while the rate of decomposition and product distribution for pure potassium perchlorate was the subject of a study by Bircumshaw and Phillips [7]. The advent of modern thermoanalytical techniques led to additional studies on both the catalyzed and uncatalyzed reactions by Marvin and Woolaver [8], Gordon and Campbell [9], Markowitz and Boryta [10–12], and Anderson and Freeman [13]. Further investigations into the decomposition processes include those of Stern and Bufalini [14], Simchen [15] and Gaidis [16]. Infra-red spectroscopic analysis was also applied to the study of perchlorate decomposition in a potassium chloride matrix where the reaction was determined to obey second order rate laws [17]. Freeman *et al.* [18–20] discussed the catalytic decomposition of perchlorates in terms of fundamental molecular properties and correlated the catalytic activity with the electronic and solid state properties of the metal oxide semiconductors.

The purpose of the current study was to gauge the relative catalytic effectiveness of various metal oxides on the thermal decomposition of potassium perchlorate and to determine the Arrhenius parameters for the catalyzed processes.

Experimental

The thermal data used in this study were obtained with a DuPont Model 900 Thermoanalyzer with the Model 950 Thermobalance accessory. A dynamic argon atmosphere was maintained at a flow rate of approximately 40 ml/min while heating rates of 5° to 100° min⁻¹ were utilized.

All chemicals were commercially supplied reagent grade materials and were used without additional purification or analysis. The individual constituents for the metal oxide/potassium perchlorate mixtures were reduced and sieved prior to mixing with the fraction passing through a number 270 mesh sieve being retained. The mixtures were prepared to microgram precision using a Mettler microbalance with blending accomplished by grinding the components together in an agate mortar and pestle for a minimum of fifteen minutes followed by repeated sieving. Care was taken to avoid loss of material during the sieving process and the final mixtures were inspected with an optical microscope for the appearance of homogeneity.

The rate curves were constructed from isothermal measurements of the weight loss of metal oxide/ potassium perchlorate samples as a function of time. Decomposition prior to achieving the isothermal condition was also measured and applied as a correction factor in the data reduction. Temperatures were monitored at random intervals during the decomposi-

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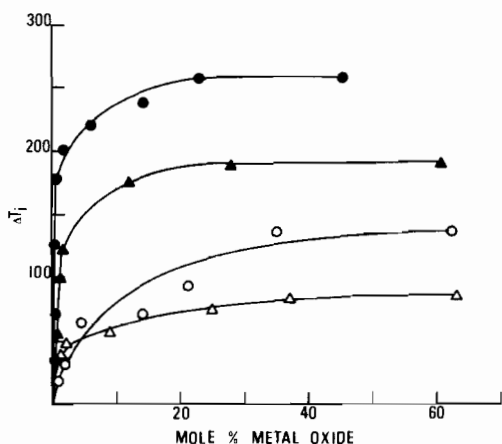
Fig. 1. Decomposition temperature of potassium perchlorate as a function of Co_2O_3 (●), MnO_2 (▲), ZnO (○), and TiO_2 (△) concentrations.

tion with a chromel–alumel thermocouple positioned near the surface of the sample.

Results and Discussion

The initial phase of the study consisted of measuring the change in the 'decomposition temperature' of potassium perchlorate as a function of metal oxide content for selected metal oxides. This decomposition temperature was derived from the temperature of initial deflection, T_i, of thermogravimetric traces of the decomposition process. The change in the decomposition temperature of pure potassium perchlorate upon addition of various metal oxides was calculated by $\Delta T_i = T_i(KClO_4) - T_i(mixture)$. However, since this temperature was found to vary with the heating rate employed, thermogravimetry curves were obtained for each mixture at three or more heating rates and the measured ΔT_i values were extrapolated to a zero heating rate. Figure 1 shows the relation between the quantity of metal oxide contained in the mixture and the magnitude of its catalytic effect as evidenced by ΔT_i. Inspection of the curves gives an appreciation of the minute quantities of metal oxide needed to produce a substantial effect on the decomposition of potassium perchlorate. While any quantity of metal oxide should catalyze the decomposition process, extremely minute quantities produce effects too small to be of practical consequences. However, Fig. 1 shows that less than 0.01% of metal oxides such as Co_2O_3 when properly dispersed can perceptibly alter the decomposition temperature by more than 25 K.

It should also be noted that beyond a given level of metal oxide addition, the effect produced is diminished and eventually approaches a constant value. Maximization of surface contact between the
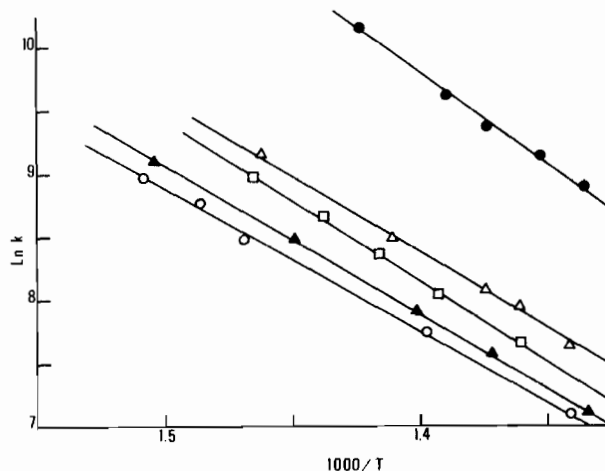

Fig. 2. Arrhenius curves for the thermal decomposition of Co_2O_3–$KClO_4$ mixtures. (●) 1.11 mol%; (▲) 6.03 mol%; (□) 14.07 mol%; (△) 22.85 mol%; (○) 45.34 mol%.

metal oxide and perchlorate might account for this effect, since addition beyond this point will not significantly improve the intimacy of the mixture to expose additional perchlorate to the catalytic action.

The second phase of the study involved the measurement of kinetic parameters for each potassium perchlorate/metal oxide mixture to elucidate the influence of metal oxide concentration on the rate of decomposition. However, these types of data are relatively difficult to obtain with great accuracy due to the complexity of the reaction system. Rates determined from weight loss measurements contain several implicit assumptions which introduce error into the calculations. For example, it is assumed that the reaction is completely specified by the mechanism

$$KClO_4 \rightarrow KCl + 2O_2$$
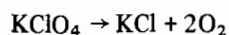
While this is the major reaction, a variety of products containing oxygen and/or chlorine are known to be formed to some extent [7].

Perhaps the most significant error in the measurements is introduced through variations in the sample temperature. Since the decomposition of potassium perchlorate is an exothermal process, significant self-heating can occur which produces an acceleration of the rate processes. Temperature differentials of up to 15 K were observed during the course of the reaction at the higher rates. Therefore, all measurements used in the calculation of kinetics parameters were made at low or moderate reaction rates to minimize the non-isothermal effect. It was also assumed that no physical change occurred during the course of the reaction which might alter the metal oxide distribution to create concentration differentials.

TABLE I. Arrhenius Parameters for the Decomposition of Potassium Perchlorate in the Presence of Various Metal Oxides.

Metal Oxide	Mol%	Log A (sec^{-1})	ΔE (Kcal)
Co_2O_3	45.34	4.9	27
TiO_2	62.00	11.5	53
ZnO	63.39	10.8	50
MnO_2	60.57	7.2	38
NiO	32.67	4.6	26
Fe_2O_3	19.77	6.9	35
Al_2O_3	27.33	12.7	60
Pure $KClO_4$		13	63

Arrhenius curves generated for Co_2O_3/$KClO_4$ mixtures, illustrated in Fig. 2, demonstrate the effect of increasing metal oxide concentration on the rates of decomposition. The Arrhenius curves for the different stoichiometries are approximately parallel over the 623 to 773 K temperature interval investigated — which is indicative of a relatively constant activation energy. The curves vary with Co_2O_3 concentration since an apparent rate constant rather than the actual rate constant is plotted. The apparent and actual constants are related by

k apparent = k actual $(M.O.)^m$

If the order is one with respect to the metal oxide concentration, m = 1, then the actual rate constant can be determined by dividing the apparent rate constants by the metal oxide concentration which will cause the parallel lines in Fig. 2 to merge. However, Fig. 1 indicates that the rate dependence on metal oxide concentration holds only for concentrations below about 25 mol%. At this concentration, surface contact between the potassium perchlorate and metal oxide is maximized so that additional oxide cannot interact to increase the extent of the catalyzed reaction. Thus, the decomposition is divided into two regions:

Below ~25 mol% metal oxide

$$-\frac{d(KClO_4)}{dt} = k(M.O.)^m (KClO_4)$$

Above ~25 mol% metal oxide

$$-\frac{d(KClO_4)}{dt} = k'(KClO_4)$$

It should also be noted that the 25 mol% limit observed in this study is an artifact of the particle size or surface area of the blend constituents and would be expected to vary with these parameters.

The Arrhenius parameters calculated from the linear regression of ln k *vs.* 1/T for each high metal oxide content mixture are listed in Table I. All measurements used in the calculations were made at moderately low temperatures since the data exhibited considerable deviation from the linear regression at higher temperatures. This could be attributed to the exothermic self-heating mentioned previously, or to a change in the decomposition mechanism as melting becomes significant. The temperature at which this deviation occurred varied according to the catalyst used, but no mixtures gave usable data above about 800 K.

While most of the data used in the calculation of the Arrhenius parameters was relatively consistent, the mixtures containing TiO_2 and ZnO gave more deviation than the other mixtures with experimental error in the activation energies and pre-exponentials skewed toward larger values. No factors which would explicitly account for this trend were observed, although the mode of decomposition may have been different for TiO_2 and ZnO mixtures compared to the other metal oxides. Microscopic observations of the decomposition process on a hot stage in a static environment revealed traces of a green-yellow gas on the surface of the mixtures containing TiO_2 and ZnO which quickly dissipated upon opening the cell. The presence of this gas was not detected during the decomposition of the other metal oxide mixtures although it may have been obscured by the dark color of the mixtures.

In order to explain the nature of the interaction of the metal oxides with the potassium perchlorate, various physical properties and electron configurations were correlated with the observed ranking of catalytic effectiveness. No significant trend could be unequivocally established although the catalytic effectiveness generally increased as the reported degree of *p*-type semiconductivity increased as suggested by Freeman *et al.* [20]. However, further study is required to establish a mechanism to account for the catalytic properties of the n-type as well as the *p*-type semiconductors if this property is actually a significant indicator of catalytic effectiveness.

References

1 F. E. Brown, J. A. Burrows, and H. M. McLaughlin, *J. Am. Chem. Soc.*, *45*, 1343 (1923).
2 J. A. Burrows and F. E. Brown, *J. Am. Chem. Soc.*, *48*, 1970 (1926).
3 H. M. McLaughlin and F. E. Brown, *J. Am. Chem. Soc.*, *50*, 782 (1928).
4 C. E. Otto and H. S. Fry, *J. Am. Chem. Soc.*, *46*, 269 (1924).
5 H. A. Neville, *J. Am. Chem. Soc.*, *45*, 2330 (1923).
6 C. E. Otto and H. S. Fry, *J. Am. Chem. Soc.*, *45*, 1134 (1923).

7 L. L. Bircumshaw and T. R. Phillips, *J. Chem. Soc.,* *142,* 703 (1953).

8 G. G. Marvin and L. B. Woolaver, *Ind. Eng. Chem., Anal. Ed., 17,* 474 (1945).

9 S. Gordon and C. Campbell, *Anal. Chem., 27,* 1102 (1955).

10 M. M. Markowitz and D. A. Boryta, *J. Phys. Chem., 69,* 1114 (1965).

11 M. M. Markowitz and D. A. Boryta, *J. Phys. Chem., 64,* 1711 (1960).

12 M. M. Markowitz, D. A. Boryta, and H. Stewart, *J. Phys. Chem., 68,* 2282 (1964).

13 D. A. Anderson and E. S. Freeman, *Nature, 195,* 1297 (1962).

14 K. H. Stern and M. Bufalini, *J. Phys. Chem., 64,* 1781 (1960).

15 A. E. Simchen, *J. Phys. Chem., 65,* 1093 (1961).

16 J. M. Gaidis, *J. Chem. Ed., 40,* 78 (1963).

17 I. C. Hisatsune and D. G. Linnehan, *J. Phys. Chem., 74,* 4091 (1970).

18 D. A. Anderson and E. S. Freeman, *J. Inorg. Nucl. Chem., 27,* 1470 (1965).

19 E. S. Freeman and D. A. Anderson, *Nature, 206,* 378 (1965).

20 W. K. Rudloff and E. S. Freeman, *J. Phys. Chem., 74,* 3317 (1970).