

Summary

1. Comparison of results obtained for the alkaline permanganate oxidation of propionate- 1-C^{14} with those for the corresponding C^{11} compound show certain differences: 90% of the activity is incorporated in the oxalate fraction in the former case compared to 87% for the latter. Since these differences may be within the limits of experimental error, their significance is hard to assess. Thus the presence of a measurable isotope effect in this case could not be definitely determined.

2. Since pyruvate has been postulated as an

intermediate in propionate oxidation, the behavior of pyruvate- 2-C^{14} in alkaline permanganate was investigated. Under these conditions approximately 80% of the pyruvate is transformed into oxalate and carbonate, with the former retaining all the activity; 20% of the pyruvate is decarboxylated, however, yielding labeled acetate and inactive carbonate. Thus, decarboxylation is a minor pathway in pyruvate oxidation under these conditions and has to be taken into consideration when discussing the mechanism of propionate oxidation as well.

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[CONTRIBUTION FROM THE DEPARTMENT OF ORGANIC CHEMISTRY OF THE HEBREW UNIVERSITY, AND THE LABORATORIES OF THE SCIENTIFIC DEPARTMENT, MINISTRY OF DEFENCE]

The Oxidation of Carbon Black by Solid Potassium Perchlorate

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Introduction

Combustible mixtures of solids have been described as giving a self-sustaining reaction only at temperatures higher than the decomposition point of the oxidant¹ or after initiation by local ignition.² In several cases, a surprisingly low

temperature of initiation has been observed,³ and although no information is available as to the mechanism and kinetics of the initiation reaction, Schneider⁴ has assumed that reaction of mixtures of organic substances and inorganic oxidants is dependent on the primary liberation of free oxygen by decomposition of the oxidant.

We studied the behavior of the mixture of potassium perchlorate and carbon black. In the temperature range of 320–385°, it reacted according to the equation $\text{KClO}_4 + 2\text{C} = 2\text{CO}_2 + \text{KCl}$. In most cases, 60–90% of the mixture reacted in this manner smoothly in the course of five hours.

Experimental

The apparatus consisted of an electric furnace and a cylindrical glass reaction chamber with a well for the thermocouple; this was connected to a sensitive millivoltmeter permitting readings within 0.5°. An elongated part of the reaction chamber protruded from the furnace; a glass spoon joined to a small steel block could be introduced into the reaction chamber or withdrawn from it into the cold part of the apparatus by means of an electromagnet. The apparatus was connected to a mercury manometer, a rotary vacuum pump and an Orsat-type gas analyser.

Preparation of Samples.—Pure potassium perchlorate, ground to 200 mesh, and a commercial carbon black (average diameter of particles, 0.005 mm.) were used. The latter, after drying at 120°, contained about 0.5% of volatile matter (at 300° *in vacuo*) and 1.5% of ash, consisting of alkali sulfates and carbonates and traces of iron.

The components were thoroughly mixed in the desired proportions (for each mol. of carbon black: 0.25; 0.50; 0.75; 1.0 and 5.0 mol. of perchlorate), wetted with about 5% water and pressed into tablets under a pressure of 600 atm. The tablets were dried for four hours at 120° and degassed at 250° *in vacuo*. This procedure gave reproducible results and no change in reaction rate was observed

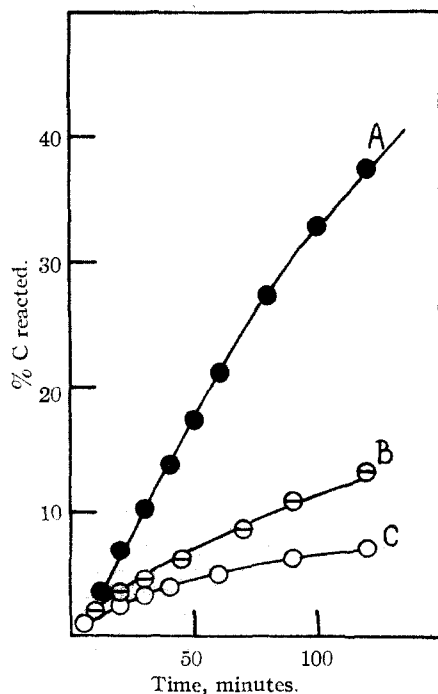


Fig. 1.—Reaction rates of carbon-potassium perchlorate (1:0.5 mole) mixtures at 367°: A, standard sample, mixed, wetted and pressed at 600 atm.; B, same mixture, ground together but not pressed; C, mixed by shaking only.

(1) Davis and Hardesty, *Ind. Eng. Chem.*, **37**, 59 (1945).

(2) Taylor, *Ind. Chemist*, **24**, 289 (1948); U. S. Patent 2,159,234 C. A., **33**, 7116 (1939).

(3) Taradoire, *Documentation Sci.*, **6**, 232 (1937) [C. A., **32**, 1455 (1938)]; Heertjes and Houtmann, *Chem. Weekblad*, **38**, 85 (1941) [C. A., **36**, 5349 (1942)]; Heinrich, *Forstarchiv*, **16**, 189 (1940) [C. A., **36**, 2146 (1942)]; Elliott, U. S. Bur. Mines Repts. Invest. No. 4244 (1948) [C. A., **42**, 3179 (1948)].

(4) Schneider, *Z. ges. Schiess u. Sprengstoffw.*, *Nitrocellulose*, **38**, 147 (1943) [C. A., **38**, 2210 (1944)]; *ibid.*, **38**, 125 (1943) [C. A., **38**, 2823 (1944)].

when the tablets were stored for prolonged periods. Omission of the wetting step decreased the reproducibility of the results.

Curve A in Fig. 1 shows the reaction rate of a standard sample. If the components are ground together in a mortar, but not pressed, the rate of the reaction is greatly decreased (curve B); greater decrease is found if the mixing is effected only by prolonged shaking in a test-tube (curve C).

Experimental Procedure.—The weighed sample (50–200 mg.) was placed in the glass spoon and the apparatus evacuated to a pressure less than 1 mm. At the desired reaction temperature, the spoon was introduced into the reaction chamber, care being taken that the sample was as near as possible to the junction of the thermocouple. The temperature was kept constant within 1° for five hours and the rise of pressure was measured to 0.25 mm., frequently at the beginning, and every 20–30 minutes later. The weight of the sample was chosen so as to give a final pressure of 100–150 mm. After five hours the reaction was interrupted by withdrawing the spoon to the cold part of the apparatus. The liberated gas was analyzed for carbon dioxide, carbon monoxide and oxygen, the weight loss of the sample was determined, and it was analyzed for chloride and chlorate ion. If the oxidation was slow (below 400°),⁵ the gas was found to be pure carbon dioxide and the solid free from potassium chlorate. The weight of carbon dioxide corresponded within 1–2% of the weight loss of the sample and was equivalent to the amount of potassium chloride found in the residue.

Reaction Rates of Various Mixtures of Constant Temperature.—In Fig. 2, curves A, B, C, D and E show the reaction rates at 367° (640°K.) of mixtures containing

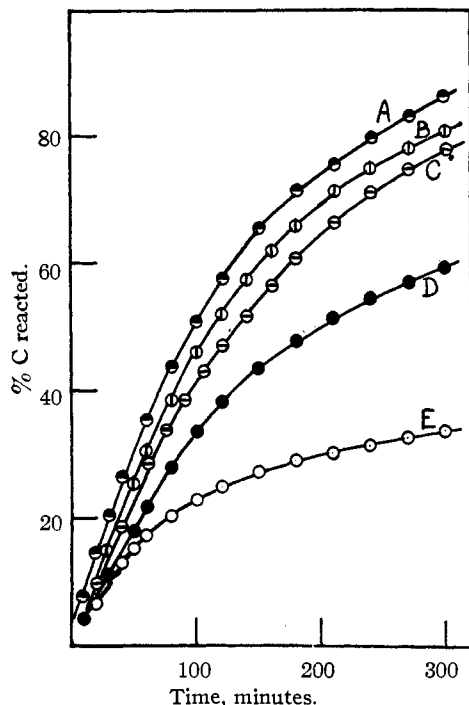


Fig. 2.—Reaction rates of various carbon–potassium perchlorate mixtures at 367° : 1 mol. of carbon—: A, 5.0 mol. of potassium perchlorate; B, 1.0 mol. of potassium perchlorate; C, 0.75 mol. of potassium perchlorate; D, 0.5 mol. of potassium perchlorate; E, 0.25 mol. of potassium perchlorate.

(5) At temperatures above 400° , the sample ignited spontaneously and the gas consisted of about 60% carbon dioxide, 40% carbon monoxide and traces of oxygen.

5.0, 1.0, 0.75, 0.50 and 0.25 moles of perchlorate, respectively, per mole of carbon. The experimental points indicate the percentage of carbon which reacted at any given time.

Reaction Rates at Different Temperatures.—Figure 3 shows the reaction of 0.25 mole of perchlorate with 1.0 mole of carbon at 385 , 367 , 345 and 320° , respectively (curves A, B, C, D). Obviously in this mixture only 50% of the carbon can react.

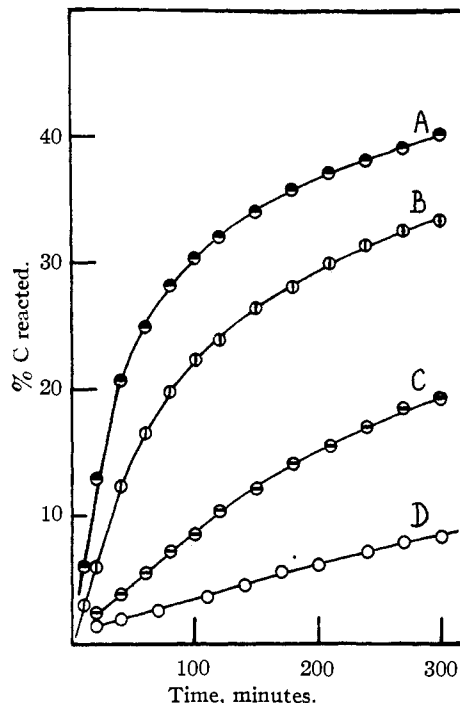


Fig. 3.—Reaction rates of a mixture of 1 mol. of carbon with 0.25 mol. of potassium perchlorate at different temperatures: A, 385° ; B, 367° ; C, 345° ; D, 320° .

Control Experiments.—Curve A in Fig. 4 shows the reaction of an equimolecular mixture at 367° under an initial pressure of 136 mm. of carbon dioxide. Curve A is practically identical with curve B in Fig. 2, showing that the carbon dioxide has no measurable effect on the reaction rate although it is a reaction product.

In the experiment illustrated by curve B in Fig. 4, which refers to a mixture of 0.5 mole of perchlorate with 1.0 mole of carbon, the reaction was interrupted after sixty minutes by withdrawing the sample to the cold part of the apparatus, and continued after a lapse of 30 minutes. Graphical elimination of the interruption results in curve C, which is identical with curve D in Fig. 2.⁶

Discussion

The reactions described take place at temperatures considerably below the decomposition temperature of potassium perchlorate (510°).⁷ Furthermore, they do not possess an induction period followed by a period of acceleration ("S"-

(6) This experiment shows that although the reaction is exothermic the heat liberated is dissipated and the temperature of the sample does not rise appreciably above the measured temperature of the reaction chamber. Otherwise, the reaction after interruption would be slower than in the corresponding experiment without interruption. The above results, incidentally, prove that no energy chains are involved in the reaction.

(7) Marvin and Woolaver, *Ind. Eng. Chem., Anal. Ed.*, **17**, 474 (1945).

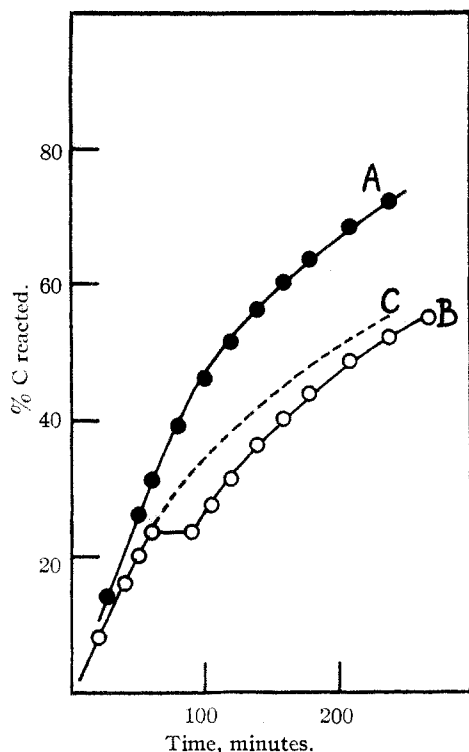


Fig. 4.—A, Reaction of 1 mol. of carbon with 1 mol. of potassium perchlorate at 367°, under an initial pressure of 136 mm. of carbon dioxide. B, Reaction of 1 mol. of carbon with 0.5 mol. of potassium perchlorate; heating interrupted after 60 min. and continued after a lapse of 30 minutes (367°). C, Graphical elimination of the interruption in curve B.

curve) as normally found in the thermal decomposition of solids.⁸ It is, therefore, unlikely that the initial reaction is the decomposition of perchlorate to chloride and free oxygen, the latter attacking the carbon black.

The first part of the reaction curves obtained could be represented *formally* by a second order equation

$$dx/dt = k_1(a - x)(b - 0.5x) \quad (1)$$

where a and b are the initial amounts of carbon and potassium perchlorate, x the amount of carbon dioxide and $0.5x$ the amount of potassium chloride at the time t , k_1 a pseudo-constant, the numerical value of which depends upon the "concentration" of the reactants. Figure 5 shows the values of k_1t obtained by integration of equation (1) plotted against the corresponding values of t for different mixtures at 367°. In all cases, the experimental points lie on a straight line at the beginning of the reaction; with a relatively high amount of perchlorate, this is true for the whole reaction line D in Fig. 5.

(8) Coppock, Colvin and Hume, *Trans. Faraday Soc.*, **27**, 283 (1931); Fischbeck and Spingler, *Z. anorg. allgem. Chem.*, **241**, 209 (1934); Garner and Hailes, *Proc. Roy. Soc. (London)*, **A139**, 576 (1933). Discussion on chemical reactions involving solids, *Trans. Faraday Soc.*, **34**, 821-1088 (1938).

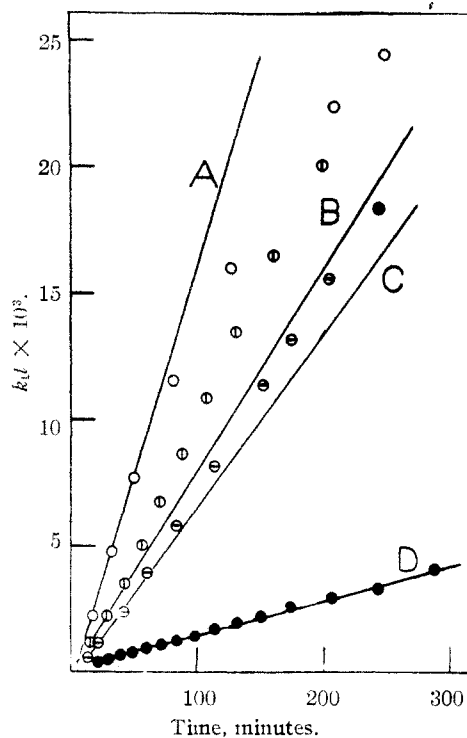


Fig. 5.—Values of k_1t calculated from $dx/dt = k_1(a - x)(b - 0.5x)$ (Equation 1) for different mixtures at 367°: 1 mol. of carbon: O, 0.25 mol. of perchlorate (A); ⊕, 0.50 mol. of perchlorate (B); ⊖, 1.0 mol. of perchlorate (C); ●, 5.0 mol. of perchlorate (D).

The deviation from the straight line in the second part of the reaction may be ascribed to an inhibiting influence of the potassium chloride formed as carbon dioxide had no influence on the reaction rate. The equation (1) is transformed into

$$\frac{dx}{dt} = k_2 \frac{(a - x)(b - 0.5x)}{0.5x} \quad (2)$$

The values of k_2t , plotted against t (Fig. 6), lie on a straight line for the second part of the reaction. The lower the relative amount of potassium perchlorate, the smaller the value of t at which the line becomes straight.

It may seem surprising that an equation holds in which the mass of the reactants and not their surface area appears. However, this is not entirely unusual for the thermal decomposition of solids.⁹

The values of the pseudo-constants k_1 and k_2 are given in Table I.

The critical increment of the Arrhenius equation was calculated for the mixture 100:25 (1.0 mole carbon: 0.25 mole potassium perchlorate) both from the values of $\log k_1$ and $\log k_2$ plotted against $1/T$ (°K.) and also from the plot of $\log t$ (from Fig. 3) against $1/T$ (°K.), taking t

(9) Garner, *Trans. Faraday Soc.*, **34**, 944 (1938).

TABLE I

NUMERICAL VALUES OF THE PSEUDO-CONSTANTS k_1 AND k_2

a (carbon)	b (KClO ₄)	T , °K.	$k_1 \cdot 10^3$	$k_2 \cdot 10^5$
100	25	640	162	107
100	50	640	79	220
100	100	640	69	266
100	500	640	14	53
100	25	618	41	24
100	25	640	162	107
100	25	658	402	218

as the time needed at various temperatures for 4, 8, 20 and 30% reaction of carbon, respectively. In all three cases the values obtained were 40 ± 4 kcal.

These results suggest the following reaction scheme: In the *first part* of the reaction where the absolute velocity dx/dt is almost constant there is no inhibition by the potassium chloride formed. This could be due to two causes: (a) The potassium chloride does not cover the surface of the perchlorate, but forms separate crystals in the spaces between the perchlorate particles. The reaction temperature is high enough to permit migration of the chloride molecules to randomly formed nuclei of crystallization.

(b) Any inhibition by the chloride in this phase is compensated by an increase in the number of "active patches" brought about by the disintegration of the surfaces of the components.¹⁰

In the *second part* of the reaction, as the amount of chloride increases, it exerts a marked inhibition, probably by diminishing the contact area of the reactants.

The values of the pseudo-constants depend not only on temperature and relative amounts of components, but also on factors such as the mass/area ratio of the reactants, the mobility of the reacting molecules and the products, and the history of the samples. It could not be expected that a simple equation exists containing a common constant for different initial values of the components.

(10) Taylor, *Proc. Roy. Soc. (London)*, **A108**, 105 (1925); Adam, "The Physics and Chemistry of Surfaces," 3rd ed., p. 234.

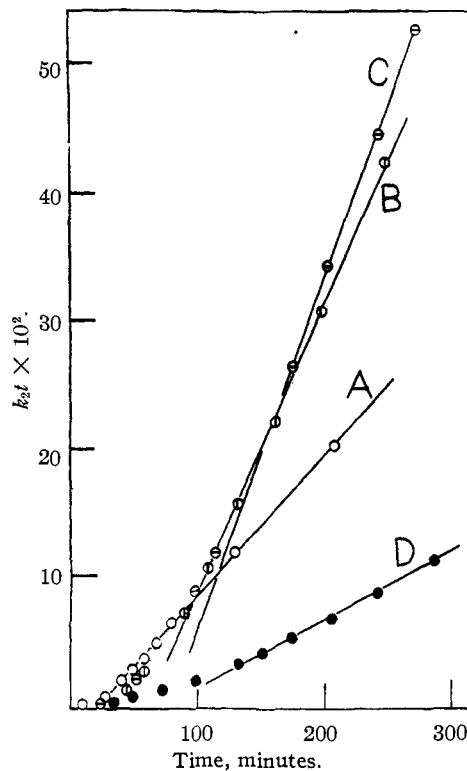


Fig. 6.—Values of k_2t calculated from $dx/dt = k_2(a - x)(b - 0.5x)/0.5x$ (Equation 2) for different mixtures at 367° : 1 mol. of carbon—: O, 0.25 mol. of perchlorate (A); \odot , 0.5 mol. of perchlorate (B); \ominus , 1.0 mol. of perchlorate (C); \bullet , 5.0 mol. of perchlorate (D).

Summary

The reaction between solid potassium perchlorate and carbon black was studied with different initial amounts (a) and (b) of the reactants in the temperature range of 320 – 385° . Two equations, $dx/dt = k_1(a - x)(b - 0.5x)$ and $dx/dt = k_2(a - x)(b - 0.5x)/0.5x$, respectively, were found to correspond to the first and second parts of the experimental curves.

Explanations for these results are suggested.

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