Reactions between Solids. Part II. The Reaction between Potassium Perchlorate, Potassium Iodate, and Different Forms of Carbon.*

By Eliahu Hoffmann and Saul Patai.

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The influence of various physical factors such as wetting, pressure in preparation, ageing of tablets, particle size of components, temperature of reaction, and relative quantities of reactants was investigated in the solid–solid reaction of potassium perchlorate and potassium iodate with different forms of carbon. A new empirical rate equation $dx/dt = k(a - x)^{2/3}/x^{1/3}$ is proposed and it is shown to be valid for a wide range of different stoicheiometrical mixtures. Factors influencing the reaction rate are discussed.

In Part I * the reaction between solid potassium perchlorate and carbon black was studied with varying initial amounts of the reactants, in the temperature range of 320—385° c. The aim of the present paper was to determine the influence of various physical factors involved on the course of this reaction, using different forms of carbon (Nuchar and sugar charcoal) and also, for comparison, with potassium iodate as the oxidant in some cases.

Experimental.

The apparatus and the experimental procedure have been described elsewhere (Patai, *Experientia*, 1952, **8**, 76).

Preparation of Standard Samples.—Pure potassium perchlorate (Baker's Analysed) of determined particle size was prepared by using American Bureau of Standards sieves. The potassium iodate (Baker's Analysed) was ground to pass a 200-mesh B. of S. sieve. The Nuchar (Eastman Kodak Co.) had an average particle diameter of 0·01 mm. and left, on ignition, 3·5% of residue, of which 0·45% was iron oxide, 0·5% silicon dioxide, and the balance calcium sulphate. The average diameter of the particles of sugar charcoal was 0·02 mm. and the residue of 0·86% which was left on ignition consisted of magnesium and calcium sulphates. It also contained some very strongly absorbed or possibly chemically bound water, which was eliminated at 500° *in vacuo*.

The reactants were thoroughly mixed in various stoicheiometric proportions (the total mixture weighing about 1 g.), wetted with three drops of distilled water, pressed into tablets under a pressure of 2250 kg./cm.^{2} and dried at 120° for 4 hr. Samples of about 50 mg. taken from these tablets were used for the experiments. Each curve shown in the Figures represents

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* Part I, Patai and Hoffmann, *J. Amer. Chem. Soc.*, 1950, **72**, 5098.

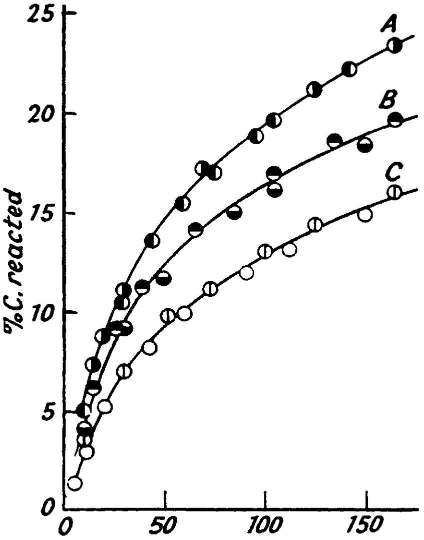
at least two or three runs made under identical conditions. The average experimental error was 1—2%.

Influence of Wetting.—Samples prepared without the addition of water were mechanically weaker and tended to disintegrate on handling. Reaction rates obtained with such samples were constantly lower than those obtained with standard samples. The difference between values obtained after 2—4 hours' reaction time (10—15% reaction) amounted to 2—4% (*i.e.*, a relative difference of 20—25%).

Influence of the Pressure of Preparation of the Samples.—Tablets prepared under a pressure of 1125 kg./cm.^{2} showed lower reaction rates than those prepared under standard conditions (2250 kg./cm.^{2}), differing from the latter by about the same amount as the unwetted from the wetted samples.

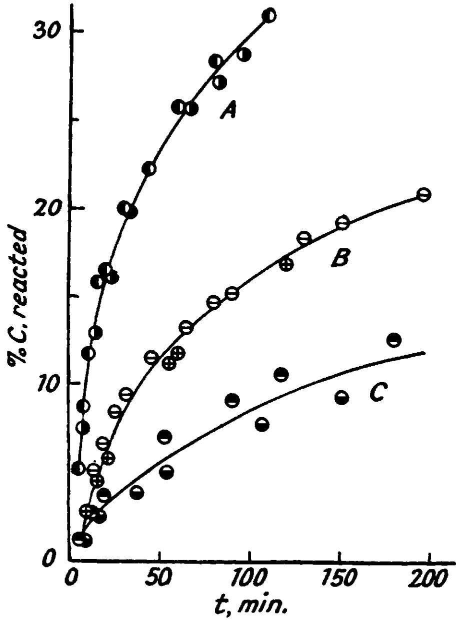
Ageing.—After 14 days' storage of the samples the reaction rates diminished slowly, reaching the values characteristic of the unwetted samples after 6—9 months. Aged samples were also more brittle and tended to disintegrate spontaneously.

FIG. 1. *Influence of the size of the potassium perchlorate particles on the reaction of* 1 *atomic equiv. of Nuchar with* 0·5 *mol. of potassium perchlorate, at* 343°



A, 200—230; *B*, 170—220; *C*, 140—170 mesh.

FIG. 2. *Influence of the temperature on the reaction of* 1 *atomic equiv. of Nuchar with* 0·5 *mol. of potassium perchlorate* (200—230 *mesh*).



A, 367; *B*, 343; *C*, 319°.

Influence of Particle Size.—Curves *A*, *B*, and *C* in Fig. 1 show the reaction rates, at 343°, of standard samples prepared with Nuchar and potassium perchlorate of different particle sizes (average diameters, 0·068, 0·081, and 0·0965 mm.). Each curve represents an average of four runs, with the experimental points of two runs only shown for each curve.

Experiments at Different Temperatures.—Fig. 2 shows the reaction rates of standard samples from Nuchar and potassium perchlorate of 200—230 mesh, at 367°, 343°, and 319°.

Experiments with Different Relative Amounts of the Reactants.—(a) *Experiments with potassium perchlorate.* Fig. 3 shows the rates of the reaction of potassium perchlorate in mixtures of 1 atomic equiv. of Nuchar with 2, 1, 0·5, and 0·25 mols. of perchlorate (200—230 mesh), at 343°. Similar curves were also obtained by measuring the rates of the reaction, at 367°, of 1 atomic equiv. of sugar charcoal with 2, 1, 0·5, and 0·25 mols. of potassium perchlorate, respectively.

(b) *Experiments with potassium iodate.* The reaction rates were measured, at 379°, of 1 atomic equiv. of sugar charcoal with 4/3, 2/3, and 1/3 mols. of <200 mesh potassium iodate. The curves obtained were again of the type shown in the previous Figures.

In all these oxidations carbon dioxide was the only gaseous product found. This was shown both by direct analysis of the gas evolved and by comparison of the weight loss of the sample with the weight loss calculated from the volume of the gas produced, the latter being assumed to be pure carbon dioxide.

DISCUSSION.

Physical factors are known to influence solid–solid reactions, but the nature of this influence has rarely been determined. Different crystalline forms of a reactant show different reactivities owing to their different energy contents and surface areas; thus amorphous seem to be generally more reactive that crystalline modifications. It is, therefore, clear that even the mode of preparation of the samples influences the reaction rates (Hedvall, *Z. angew. Chem.*, 1931, **44**, 781). The reaction of potassium perchlorate in our case takes place at temperatures above its transition point (299°), at which a change from a rhombic to a face-centered cubic lattice occurs (Vorlander and Kaascht, *Ber.*, 1923, **56**, 1157). Such lattice changes enhance the reactivity of solid substances (Hedvall, *Z. phys. Chem.*, 1926, **123**, 33).

The variations in the reaction rates of stoicheiometrically identical samples, due to different physical factors such as pressure of preparation, wetting, ageing, and particle size, will mainly be caused by variation in the contact area of the reactants. In the case of ageing there may also be a very slow reaction at room temperature. Even if the occurrence of such a reaction could not be proved by ordinary analytical means, only an extremely thin layer of potassium chloride at the interfaces of the carbon and the potassium perchlorate may be necessary in order to block, at least partially, the reactive spots. The residual moisture left in the samples after drying may also lower the reaction rate, because it may permit the small particles of potassium perchlorate to recrystallise and form larger aggregates. (These traces of moisture are eliminated from the samples only by repeated degassing *in vacuo* at 250°.)

In any case, the influence of the particle size on the reaction rate, as shown in Fig. 1, proves that the rate depends primarily upon the available surface areas. However, the relation between surface area and reaction rate does not seem to be simple. Similar solid–solid heterogeneous systems have been investigated, *e.g.*, by Tammann and by Jander (Tammann, *Z. anorg. Chem.*, 1926, **149**, 21; Jander, *ibid.*, 1927, **163**, 1; 1927, **166**, 31; 1927, **168**, 113). These authors based their treatment of the solid–solid reaction rates on considerations of diffusion processes. During most solid–solid reactions a product layer is formed which separates the reactants and thus the continuation of the process depends on the diffusion of at least one of the reactants through this layer. According to Tammann (*ibid.*, 1920, **111**, 78) the rate of growth of the product layer is $\mathrm{d}y/\mathrm{d}t = k/y$ (Eq. 1*a*), where y is the thickness of the product layer; the integrated form of this equation is $y^2 = 2kt$ (Eq. 1*b*).

Assuming the rate of growth of the product layer to be proportional to the reaction rate, Jander applied equation 1*b* to the reaction of powder mixtures with one of the reactants in great excess over, and of much smaller particle size than, the second component. Jander has shown that for these cases the following relation applies:

$$y = r\{1 - \sqrt[3]{[(100 - x)/100]}\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (\text{Eq. } 2)$$

where y is again the thickness of the product layer, r is the radius of the original particle, and x is the amount of the product at time t. Substitution of the value of y from Eq. 2 into Eq. 1*b* gives

$$\{1 - \sqrt[3]{[(100 - x)/100]}\}^2 = 2kt/r^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (\text{Eq. } 3)$$

which was shown by Jander to be correct for various solid–solid reactions in which a homogeneous product layer is formed.

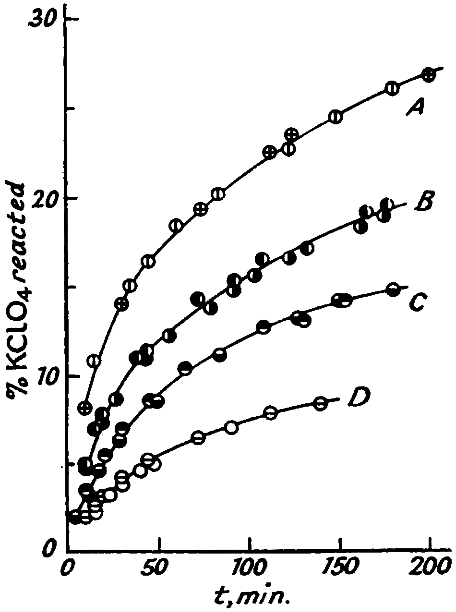
In our case, the amount of the solid product, *i.e.*, the amount of the potassium chloride formed, can be calculated directly and continuously from the amount of carbon dioxide evolved in accordance with the equation $KClO_4 + 2C \longrightarrow KCl + 2CO_2$, and the carbon can be taken, at least in most of our experiments, as the component present in excess, owing to the much smaller size of its particles. Indeed, in good accord with Eq. 3, a plot of the left-hand side of Eq. 3 as a function of the time gives straight lines. The values of the rate coefficients k for stoicheiometrically identical mixtures of carbon (Nuchar) with potassium perchlorate of three different particle sizes, calculated from the slopes of these lines, after consideration of the factor $2/r^2$, are given in Table 1.

TABLE 1. *Values of the rate coefficients for the reaction of* 1·0 *atomic equiv. of Nuchar with* 0·5 *mol. of potassium perchlorate of different particle sizes, at* 343° (*from Fig.* 1).

Initial average radius of perchlorate particles (mm.)	Initial ratio of the carbon/ perchlorate surface area	$10^{10}k$ (cm.^{2} min.$^{-1}$)
0·0483	2120/171	2·25
0·0405	2120/203·7	2·50
0·034	2120/242·6	2·67

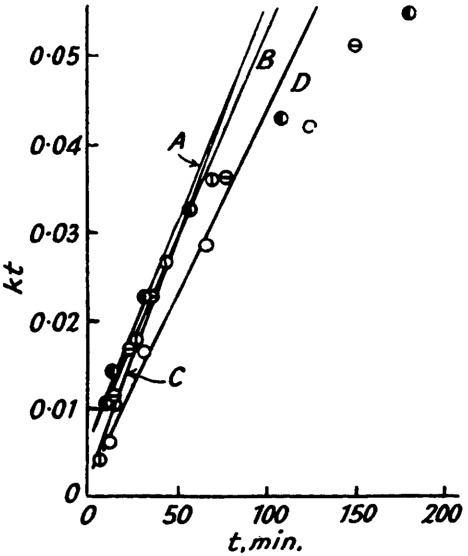
The consistency of the k values appears to be satisfactory when consideration is given to the difficulties of preparing standard mixtures. However, the above equation fails to explain the fact that reaction rates vary with the initial ratio of the reactants as shown in, *e.g.*, Fig. 3. As in all these mixtures the surface area of the carbon was very much larger than that of the perchlorate particles, there should be practically no variation in the reaction rate, at least not initially. The following empirical rate equation was found to give fairly uniform rate coefficients for stoicheiometrically different mixtures of potassium perchlorate and carbon :

FIG. 3. *Reaction of different amounts of potassium perchlorate with* 1 *atomic equiv. of Nuchar, at* 343°.



A, 0·25; *B*, 0·5; *C*, 1·0; *D*, 2·0 mols. of perchlorate.

FIG. 4. *Values of kt–t* (*from equation* 6), *calculated from the experimental runs shown in Fig.* 3.



A, 0·25; *B*, 0·5; *C*, 1·0; *D*, 2·0 mol. of potassium perchlorate.

$$dx/dt = k(a - x)^{2/3}/x^{1/3} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(Eq. 4)}$$

Here dx/dt is the rate at which potassium chloride is produced, *i.e.*, at which potassium perchlorate disappears, a is the initial quantity of perchlorate present, ***in moles per g.-atom of carbon***, and x is the amount of perchlorate which has reacted (in the same units) at time t.

In Eq. 4 the reaction rate is proportional to the surface area of potassium perchlorate, represented by the factor $(a - x)^{2/3}$. The equation thus takes into account the influence of the size of the perchlorate particles. The rate coefficient k contains a factor which is dependent on the radius r of the perchlorate particles but, as in the present study the perchlorate particle size has been generally kept constant, r does not appear explicitly in the equation. A more general form of Eq. 4 would be

$$\mathrm{d}x/\mathrm{d}t = k(a - x)^{2/3}/r^2x^{1/3}$$

By using this expression, practically coincident straight lines were obtained on plotting kt against t from the experimental curves shown in Fig. 1.

The reaction rate is furthermore dependent on the initial ratio of the reactants, as both a and x are expressed in units based on the perchlorate : carbon ratio. The factor $x^{1/3}$ represents the amount of potassium chloride formed, which must obviously appear as a divisor, as the chloride lowers the reaction rate, forming a barrier between the reactants. In the case of slabs of planar reactants pressed together, the thickness of the dividing layer (represented by y in Eq. 1a) should be proportional to x and for reactants of various shapes to x^n, where n must be smaller than unity. No theoretical explanation can be given by us for the occurrence of the power of 1/3.

Eq. 4 can be written thus :

$$kt = \int_0^x x^{1/3}\mathrm{d}x/(a - x)^{2/3} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(Eq. 5)}$$

This integral can be solved by developing it into a series, the members of which can be integrated in turn :

$$kt = 3(x^2/a)^{2/3}[0{\cdot}25 + (0{\cdot}28571x/3a) + 0{\cdot}5(x/3a)^2 + \ldots] \quad . \quad . \quad \text{(Eq. 6)}$$

For the evaluation of the experimental results it proved to be sufficient to take into consideration only the first three members of the series. Fig. 4 shows the graphical representation of kt–t according to Eq. 6, from the experimental values shown in Fig. 3 for different mixtures of potassium perchlorate and Nuchar. Very nearly coincident lines were also obtained in the same manner for the reactions of other mixtures employed in this investigation (see Table 2). Eq. 6 is valid only as long as the surface area of the carbon is large in comparison with that of the perchlorate. This can be seen for instance from the rate coefficients in Table 2, representing the reaction rate of different amounts of potassium perchlorate with carbon black.[*] In general, Eq. 6 appears to hold only for the steep portion of the reaction curves, and in the latter stages of the reaction the experimental falls below the calculated rate. Table 2 shows the values of the rate coefficients as calculated

TABLE 2. *Rate coefficients calculated from kt–t curves* (Eq. 6).

Reactants	Molar ratio oxidant : carbon	t	10^4k (min.$^{-1}$) [*]
$KClO_4$–Nuchar	0·25 : 1	343°	5·2
,, ,,	0·50 : 1	,,	5·0
,, ,,	1·0 : 1	,,	5·5
,, ,,	2·0 : 1	,,	4·4
$KClO_4$–sugar charcoal	0·25 : 1	367	4·6
,, ,,	0·50 : 1	,,	4·85
,, ,,	1·0 : 1	,,	4·5
,, ,,	2·0 : 1	,,	4·0
$KClO_4$–carbon black	0·25 : 1	367	13
,, ,,	0·50 : 1	,,	12·2
,, ,,	1·0 : 1	,,	12·1
,, ,,	5·0 : 1	,,	4·2
KIO_3–sugar charcoal	0·33 : 1	379	55
,, ,,	0·66 : 1	,,	41
,, ,,	1·33 : 1	,,	29

[*] The dimension of the rate coefficient is min.$^{-1}$, as both a and x (being expressed in moles per g.-atom of carbon) are dimensionless. As the rate expression (Eq. 4) is valid only as long as the surface area of the carbon is comparatively very large, the formal analogy of the dimension of this rate coefficient to that of a general first-order rate coefficient is not unexpected.

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[*] These rate coefficients were recalculated from the experimental results of a previous paper (Patai and Hoffmann, *loc. cit.*).

by means of Eq. 6 from *kt–t* graphs, consideration being given to the experimental points only up to about 100 minutes.

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LABORATORIES OF THE SCIENTIFIC DEPARTMENT, MINISTRY OF DEFENCE, ISRAEL.
DEPARTMENT OF ORGANIC CHEMISTRY,
THE HEBREW UNIVERSITY, JERUSALEM.

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