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RESEARCH ON SOLID STATE CHEMICAL REACTIONS

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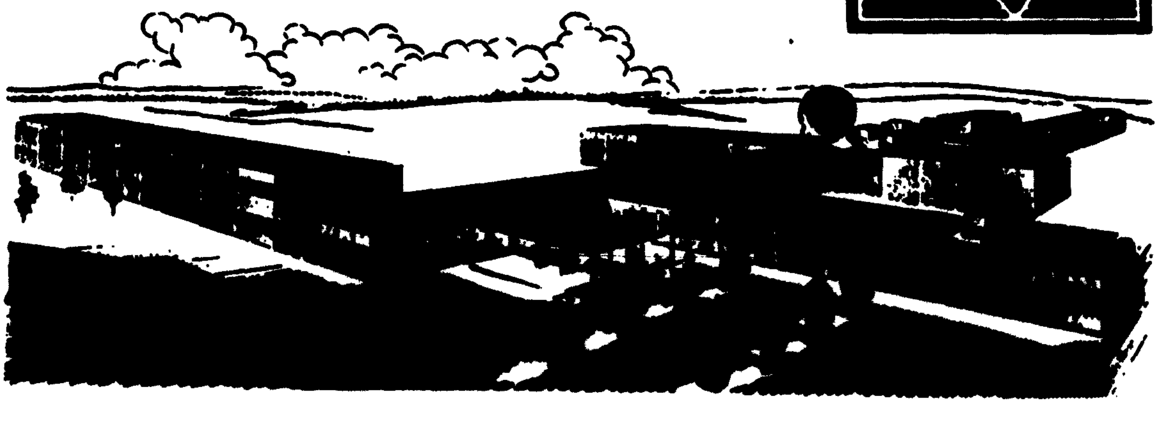

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TECHNICAL (FINAL) REPORT

Research on Solid State Chemical Reactions

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Abstract

This report describes the investigation of the solid-solid oxidation of synthetic diamond and synthetic graphite by potassium perchlorate in the presence and absence of catalysts (Part A). It also describes the oxidation reaction of high-melting organic compounds by potassium chlorate in the presence and absence of various catalysts (Part B).

This work is a continuation of research reported in several technical notes (16) and published papers (1-14).

Some unsuccessful experiments are also described briefly.

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A. The oxidation of synthetic diamond and synthetic graphite

Experimental

The experiments were carried out on tablets of 6mm diameter which had been pressed of powdered and slightly moistened ingredients at 6000 psi, dried in an evacuated chamber at $\sim 10^{-4}$mm Hg at 100°C for several hours. The tablets were weighed and inserted into the reaction chamber (3), the temperature of which was controlled by a Sunvic Resistance Thermometer Controller. The temperature of the reaction chamber was measured potentiometrically by a thermocouple, and the fluctuation of the temperature at 400°C was ±.0.6°C. The tablets, in some cases were made of mixed powders of the reactants, and in others "sandwich" like - tablets of known composition were used (see below).

The powders were mixed by a vibration mill in order to get homogenous samples.

The course of the reaction was followed by measuring the pressure of the gases liberated, the volume of the reaction chamber being kept constant (3). Analysis of chloride was performed, as a rule, on tablets taken out of the reaction chamber in the following manner: The tablet was dissolved in boiling, redistilled water and titrated with 0.05 N $AgNO_3$ using "Radiometer" automatic potentiometric titrator to a predetermined end-point. This method proved to be very accurate - the Volhard method being unsuitable because of the relatively low concentration of chloride ions present.

Materials

The oxidants and additives were of the best commercially available grade (Baker Analar). Size of particles was less than 200 mesh.

The synthetic diamond was a General Electric product. The size of its particles was less than 400 mesh. Its crystals had a cubic structure which, according to preliminary results had a type I tetrahedral structure. The analysis showed 0.5% impurities, predominantly nickel. The data are taken from a personal communication by Mr. H.B. Weaver of General Electric Company, Detroit 32 Michigan, to whom we are indebted for supplying this material.

The graphite was a BDH product, its analysis was: C - 99.1%, H - 0%, residue - 0.2% (Analysis by Mrs. M. Goldstein, The Hebrew University, Jerusalem).

This material was degased in a vacuum of 10^{-5}mm Hg at 500°C for at least 10 hours.

The labelled $KClO_4$ was a product of the Radiochemical Centre, Amersham, having a specific activity of 25.2 µc/mM and was 100% labelled.

Blanks

a) We measured the percentage of decomposition of pure oxidant tablets and of tablets consisting of a mixture of the oxidant and the additive at several temperatures in order to determine the temperature at which the decomposition was equal to about 1%. This was taken as the highest temperature at which experiments could be performed without introducing too large errors into the pure solid-solid reaction. (Table 1)

b) Various samples which were ground, mixed, pressed and dried were analysed for chloride after every separate step. No chloride was found resulting from this treatment.

c) The influence of ambient CO_2 on the reaction rate was investigated by carrying out one run at 380°C with a diamond - $KClO_4$ - V_2O_5 tablet under a pressure of 354 mm Hg of CO_2 instead of under vacuo as usual. The rate was not influenced by the presence of the CO_2, showing, as expected, that the reaction is practically irreversibl .

d) The gases liberated during the reaction were transferred into a vacuum system and their pressure was measured. A trap in the system was then cooled by liquid air and the pressure measured again. The pressure dropped from 100 mm Hg to 0.5 mm Hg which indicated that the only gas liberated in the reaction was CO_2.

Table 1

Highest possible working temperatures with various oxidant-catalyst mixtures

Oxidant	amount in milimoles	additives	amount in percent w/w	max. temp. °C	% of decomp. after 24 hrs.
$KClO_4$	1	-	-	430	1
"	3/4	V_2O_5	3%	380	0.5-1
"	1	"	3%	380	<1
"	1½	"	3%	380	<1
"	2½	"	3%	380	<1
"	3/4	$Fe_2(SO_4)_3$	3%	380	1
$KClO_3$	2/3	-	-	340	2
"	2/3	V_2O_5	3%	250	2

RESULTS

The oxidation of synthetic diamond by $KClO_4$

The dependence of the reaction rate on the ratio of the reactants was investigated. The results are shown in Table 2.

Table 2

Oxidation of synthetic diamond by $KClO_4$ (without catalyst) after 27 hours

Run No.	equivalent ratio* $KClO_4$: C**	T°C	% reaction calc'd from CO_2 pressure*
C_7	5 : 1	415	2.6
E_{3-4}	2 : 1	430	3
E_{5-6}	5 : 1	430	6;7
B_{1-2}	½ : 1	440	8
B_{3-4}	1 : 1	440	8;10
C_{9-11}	1 : 1	440	4;7
C_{1-2},B_{5-6}	2 : 1	440	7;9;12
B_{7-8}	5 : 1	440	15;17
C_{3-4}	5 : 1	440	16;17
C_{12}	1 : 1	460	9
$C_{5,13,14}$	2 : 1	460	13;13.5;9
C_{15}	5 : 1	460	20

Notes to Table 2:

*) Results showing up to about 4% reaction are unreliable, since discrepancies of this order of magnitude have been observed between the results calculated on basis of gas pressure and the more reliable results of chloride analysis.

**) One mole of $KClO_4$ is taken as equivalent to 2 atoms of carbon.

From Table 2 it is seen that the reaction rate increases as the "equivalent ratio", i.e. the ratio of $KClO_4$ to C, increases. But the maximum temperature allowed for this reaction (440°) is not high enough to give conveniently measurable rates; even with the ratio of 5:1 we got only about 17% reaction in 24 hours. We tried to examine the Arrhenius energy of activation by performing the reaction at 460°C (here the blank is about 4%) and at 430°C, 415°C. As Table 2 shows, at temperatures lower than 440°C, the results are unreliable as a rule. On the other hand, the results at 460°C are very similar to these at 440°C, indicating a very low energy of activation.

The oxidation of synthetic diamond by $KClO_4$ in the presence of catalysts.

We carried out some runs in the presence of catalysts. Like in the previous works, (10,12-14) Lewis acids as V_2O_5, $Fe_2(SO_4)_3$, $Al_2(SO_4)_3$ and metal powders (Cu, Al) proved to have catalytic activity on the reaction. According to blank experiments performed, the maximum temperature allowed here was 380°C (Table 1). Some experimental difficulties were caused by the water vapour liberated in the course of the reaction. Some of the catalysts used (e.g. $Fe_2(SO_4)_3$ and $Al_2(SO_4)_3$)were hygroscopic and did not lose their water content when dried before the reaction at 100°C in vacuo, but released it at the higher temperature of the reaction chamber. This fact is evident from the difference in the reaction percentage obtained when calculated on the basis of gas pressure, compared to the results of the chloride analysis. The best catalyst examined was V_2O_5 which is not hygroscopic and fairly efficient, and was chosen to be the standard catalyst in the other experiments. The results shown in Table 3 are corrected for the amount of water vapour pressure present in the apparatus and originating from the hygroscopic catalysts.

Table 3

Oxidation of synthetic diamond (1 equivalent) by $KClO_4$ (5 equivalents) at 380° in the presence of 2% (w/w) of various catalysts after 24 hours.

Run No.	Additive	% reaction
$D_{12,13}$	$Fe_2(SO_4)_3$	12;14
$D_{15,16}, K_{3,15}$	V_2O_5	11;12;9
K_{14}	Al	9
D_{21}, K_{12}	Cu	5
K_5	$Al_2(SO_4)_3$	5
	none	0

Other oxidants

Several experiments were carried out in order to examine the possibility of using other oxidants for the reaction. The results of the preliminary experiments with $KClO_4$ and $KBrO_3$ in the absence and presence of catalysts showed that even at the maximum temperature allowed for each composition, the reaction percents were smaller than in the parallel experiments with $KClO_4$ and were therefore abandoned.

The oxidation of graphite by $KClO_4$

In this part, the oxidation reaction of graphite by $KClO_4$ in the presence of V_2O_5 as the catalyst was investigated. The tablets for these series of experiments were made in the following manner:

a) "Mixed tablets" - these contained mixed powders of 12 mg graphite and a suitable amount of $KClO_4$ containing 3% by weight of V_2O_5 for the equivalent radios of $KClO_4$:C - ½:1, 1:1, 2:1, 3:1, and 4:1.

b) "Sandwich tablets" in which the graphite formed one layer to which, the oxidant, mixed with the catalyst was pressed in one or several layers, to one or both sides of the graphite layer.

c) "Mixed-sandwich tablets" - the same as (b) but the graphite layer was here mixed with ½ equivalent of $KClO_4/V_2O_5$. After pressing this layer, one or more additional layers of $KClO_3/V_2O_5$ were pressed onto it, on one or both sides.

Graphite was chosen because of the possibility to obtain mechanically stable tablets from it. Other forms of carbon such as Norit, sugar-charcoal, wood charcoal and bone charcoal were not suitable because the tablets were mechanically unstable and disintegrated during further handling necessary.

The oxidation of synthetic graphite by $KClO_4$ in the presence of V_2O_5 as catalyst in "mixed tablets"

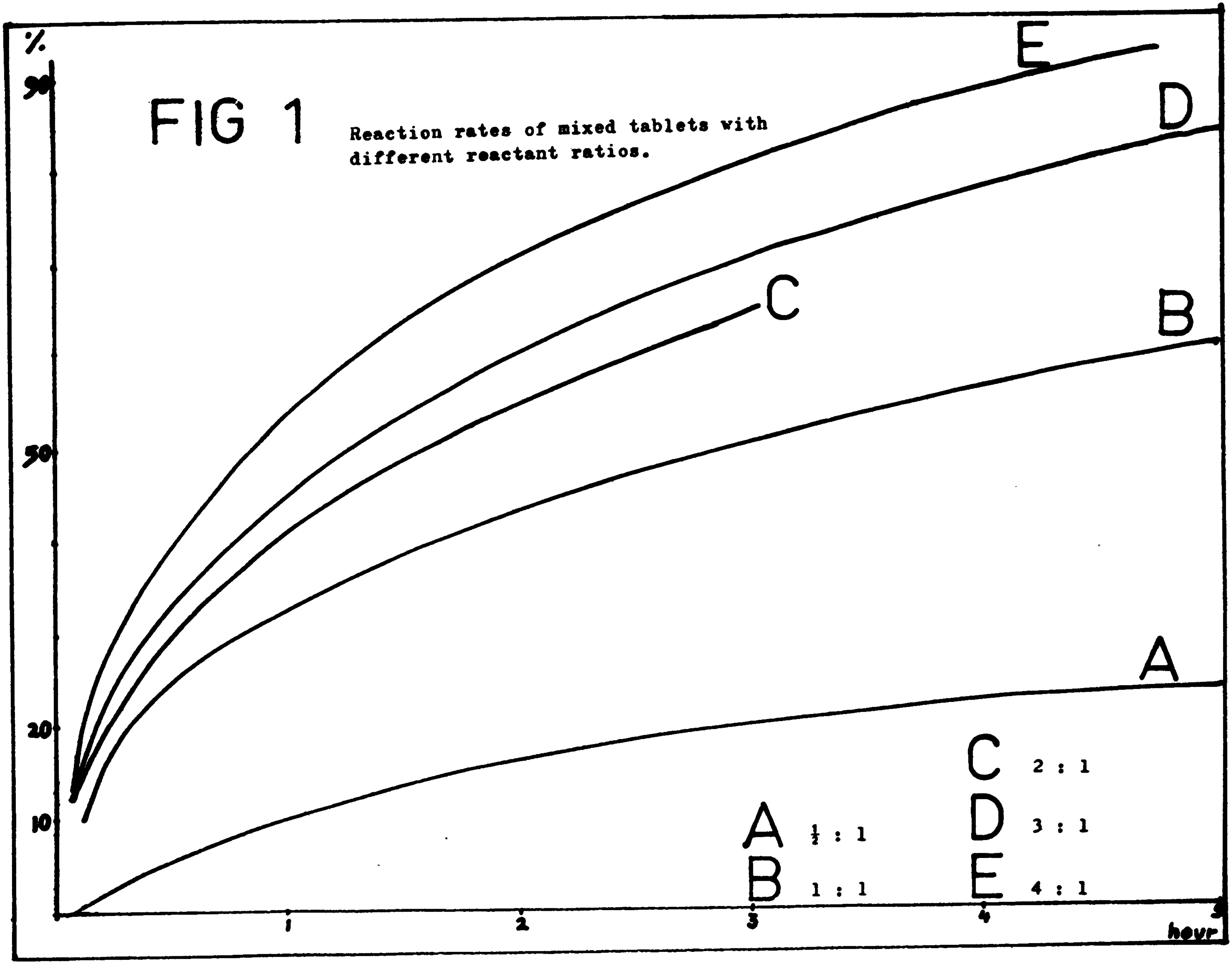
The results are shown in Table 4 and in Fig.1. Both in Table 4 and Fig. 1 each given number or drawn point respectively, represents the average value of 2-4 actual experimental determinations in separate runs.

Table 4

Comparison of selected data.

equivalent ratio $KClO_4$: C	% reaction after 3 hours	reaction interrupted			$V_{in} = \frac{x}{t}$ $\frac{\%}{hour}$ initial rate
		total hours	final % calc'd from pressure	final % calc'd titrimetrically	
½ : 1	21	18	3.3	31.2	15.5
1 : 1	50	23	88	87.8	60.5
2 : 1	65.5	3	65.5	64.6	62.5
3 : 1	78	5	91.9	89.8	83
4 : 1	80	5.5	91.5	90.2	87

FIG 1



Reaction rates of mixed tablets with different reactant ratios.

From the curves of Fig. 1 the initial rates of the reactions were calculated. The initial rate was defined as $V_{in} = \frac{x}{t}$, *i.e.*, the slope of the straight line passing through the first points of the curve, when this first part of the curve is still linear.

The jump in both the rates and the initial rates between the equivalent ratio of ½ : 1 and the others, is obvious. We tried to fit the kinetic data obtained here to various empirical equations and Jander's equation (15). The empirical equations selected were those which gave a good fit in some earlier papers (8,10,12). They are:

(a) $\frac{dx}{dt} = K \frac{(a-x)^{2/3}}{x^{1/3}}$ or in its integrated form

$$Kt = x^{4/3}(3/4a^2 + 2/7ax + 1/6x^2....)/a^{8/3}$$

(b) $\frac{dx}{dt} = K \frac{a - x}{x^{2/3}}$ or in its integrated form

$$Kt = x^{5/3}\ (3/5a^2 + 3/8ax + 3/11x^2....)/a^3$$

where: x = percentage reaction at the time t.

a = initial amount of substrate taken as 100%.

(c) Jander's equation $\frac{dy}{dt} = \frac{k}{y}$ where: y = the thickness of the product layer at the time t.

The integrated form is: $y^2 = 2kt$. Introducing for the value: $y = r(1 - \sqrt[3]{\frac{100 - x}{100}})$ into the equations where x = percent reaction at time t, and r = the radius of the particle.

Jander's equation becomes:

$$Kt = \left(1 - \sqrt[3]{\frac{100 - x}{100}}\right)^2 \quad \text{where } K = \frac{2k}{r^2}$$

Table 5 gives the calculated data according to the above three equations.

Table 5 shows that Jander's equation gives the best fit for all the runs. This equation gave also the best fit to the reaction between carbon black and $KClO_4$ in the presence of various additives(8). Equation (a) which was suitable to the data in work (10) does not fit our data. This was the case with equation (b) which was relevant in the work on the oxidation of p-divinylbenzene (12).

The oxidation of synthetic graphite in "sandwich tablets"

The dependence of the reaction rates on the ratio of the reactants was investigated also when the oxidant was mixed with the catalyst only and pressed to one or both sides of the pure graphite layer. The results are given in Table 6. Every given number represents the average value of 2-4 actual experimental determination in separate runs.

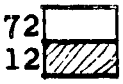
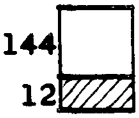
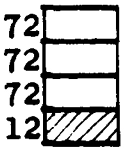
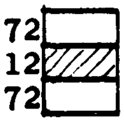
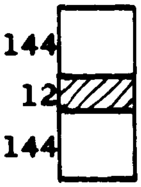
Table 5

Fit of the equation a, b, and c (see text) to the experimental data in Fig. 1

% re- action	Kt	Equivalent ratio										Equation
		½ : 1		1 : 1		2 : 1		3 : 1		4 : 1		
		t hr.	K	t	K	t	K	t	K	t	K	
10	0.78	0.94	0.83	0.08	9.75	0.08	9.75	0.08	9.75	0.06	13	
15	1.37	1.78	0.78	0.18	7.62	0.1	13.7	0.1	13.7	0.08	17.1	
20	2.05	3.38	0.60	0.26	7.9	0.19	10.8	0.15	13.6	0.13	15.7	
25	2.82	6.7	0.42	0.5	5.64	0.3	9.38	0.24	11.7	0.16	17.6	
30	3.69	11.8	0.31	0.78	4.73	0.46	8.00	0.39	9.45	0.25	14.8	(a)
35	4.62	21.0	0.22	1.26	3.66	0.66	7.00	0.55	8.4	0.35	13.2	see
40	5.65			1.7	3.32	0.88	6.45	0.75	7.53	0.5	11.3	p.11
45	6.78			2.3	2.94	11.6	5.9	1.0	6.78	0.66	10.3	
50	8.0			3.0	2.67	1.56	5.12	1.39	5.75	0.87	9.3	
55	9.30			4.0	2.32	2.04	4.54	1.71	5.43	1.1	8.45	
60	10.7			5.0	2.14	2.56	4.18	2.07	5.17	1.35	7.93	
10	0.29	0.94	0.32	0.08	3.72	0.08	3.71	0.08	3.71	0.06	4.95	
15	0.60	1.78	0.33	0.18	3.32	0.1	5.98	0.1	5.98	0.08	7.47	
20	1.00	3.38	0.30	0.26	3.86	0.19	5.3	0.15	6.7	0.13	7.75	
25	1.49	6.7	0.22	0.5	2.98	0.3	4.97	0.24	6.2	0.16	9.3	
30	2.13	11.8	0.18	0.78	2.73	0.46	4.63	0.39	5.45	0.25	8.52	(b)
35	2.84	21	0.13	12.6	2.26	0.66	4.3	0.55	5.16	0.35	8.12	see
40	3.7			1.7	2.18	0.88	4.21	0.75	4.93	0.5	7.40	p.11
45	4.63			2.3	2.01	11.6	3.99	1.0	4.63	0.66	7.03	
50	5.65			3.0	1.88	1.56	3.62	1.39	4.07	0.87	6.5	
55	7.06			4.0	1.76	2.04	3.46	1.71	4.13	1.1	6.42	
60	8.40			5.0	1.68	2.56	3.28	2.07	4.05	1.35	6.22	
%	10^4Kt	t	10^3K	t	10^2K	t	10^2K	t	10^2K	t	10^2K	
10	11.9	0.94	1.27	0.08	1.49	0.08	1.49	0.08	1.49	0.06	1.98	
15	27.8	1.38	2.01	0.18	1.55	0.1	2.78	0.1	2.78	0.08	3.46	
20	51.5	3.38	1.52	0.26	1.98	0.19	2.71	0.15	3.43	0.13	3.96	
25	84.0	6.7	1.25	0.5	1.68	0.3	2.8	0.24	3.5	0.16	5.25	
30	126	11.8	1.07	0.78	1.62	0.46	2.74	0.39	3.23	0.25	5.04	(c)
35	179	21	0.85	1.26	1.42	0.66	2.72	0.55	3.25	0.35	5.12	see
40	245			1.7	1.44	0.88	2.79	0.75	3.26	0.5	4.9	p.11
45	327			2.3	1.42	1.16	2.82	1.0	3.27	0.66	4.95	
50	426			3.0	1.42	1.56	2.73	1.39	3.06	0.87	4.9	
55	546			4.0	1.37	2.04	2.68	1.71	3.18	1.1	4.95	
60	693			5.0	1.38	2.56	2.7	2.07	3.34	1.35	5.13	

Table 6

Oxidation of graphite by $KClO_4/V_2O_5$ in "sandwich tablets" at 380°C.

equivalent ratio	symbol	percentage reaction				$V_{in} = \frac{x}{t}$ $\frac{\%}{hour}$
		1 hour	5 hour	10 hour	25 hour	initial rates.
1 : 1		1.5	3.5	5	8	0.85
2 : 1		2.0	6.5	8	15	1.5
3 : 1		3.0	8	13	25	1.8
2 : 1		3.5	8	12	16	2.1
4 : 1		5	14	20	32	4.4

As it seen from Table 1, the mass of the tablet does not influence the decomposition of $KClO_4$ in the presence of catlyst (but not substrate). These data show that in none of these cases does any local or general overheating of the tablets occur (due to the exothermicity of the decomposition or the oxidation(1). Therefore this factor can be eliminated as a possible cause of the enhanced reaction rates in "sandwich tablets" containing larger amounts of $KClO_4/V_2O_5$. The fact that thicker layers enhance the reaction rates is rather puzzling, as the direct contact between the reactants is the same in all cases when the $KClO_4$ is on one side of the graphite only, and should be twice as large in <u>all</u> the cases when the $KClO_4/V_2O_5$ mixture is pressed on both sides of the graphite layer. While we are unable to offer any exact or well founded explanation for the experimental results, they seem to fit some hypotheses advanced previously (12,13,14). According to these, it is possible that a "memory effect" operates in the decomposition of $KClO_4$ to KCl as well as in the solid-solid oxidation reaction given by $KClO_4$. If this is true, then the crystal lattice of $KClO_4$ is retained even after the removal of the oxygen atoms by decomposition or oxidation. Such a "memory" crystal lattice will attract oxygen atoms from neighbouring places in the undecomposed parts of the $KClO_4$ until a kind of equilibrium is established.

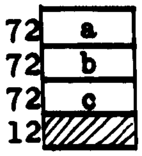
This will only happen when all the oxidizable substance (in our case graphite) is used up. According to this hypothesis a continuous gradient of sites containing various Cl/O ratios will be established and this gradient will be influenced by the absolute amount of the $KClO_4$ present in the system. The flow of oxygen from the undecomposed $KClO_4$ towards the places where the decomposition or the oxidation takes place, will be <u>faster</u> if there is a large "reservoir" of $KClO_4$ even though the latter is considerably removed from the actual reaction site.

In the case of tablets of ratio 3:1, the oxidant layer was composed of three separate layers pressed one after the other to the substrate layer. These tablets were separated after the reaction into the three separate oxidant layers, and they were each weighed and analysed for chloride. The adhesion of the separately pressed $KClO_4$ layers to each other was rather poor and they often separated spontaneously. Nevertheless, if the layers separated during the handling, but were returned on top of each other, even this contact (without applying additional pressure) was sufficient to obtain decomposition of the $KClO_4$ in these layers remote from the substrate. It seems therefore, that the "pumping" effect of the memory lattice is able to exert its influence even through a loose boundary layer. Relevant results are contained in Table 7.

Table 7 shows: 1) that in every $KClO_4$ layer the percentage of decomposition is higher than in the blank. 2) there is no reproducible "decomposition grandient" in the various layers - the percentage of decomposition, as a rule, is not decreasing when the oxidant layer is more remote from the substrate. These facts seem to indicate a migration of oxidizing material in a reasonably fast-equilibrium process, from the oxidant to the substrate. Later it will be shown

Table 7

% of chloride found by analysis in different layers of a $KClO_4$/graphite sandwich tablet, at 380°C.

time of the reaction	% of decomposition of the $KClO_4$			total % of decompoos.	Symbol
	a	b	c		
26.5	5.4	4.1	5.1	4.96	
26.5	5.7	5.5	7.85	6.34	
24	4.9	10.2	6.5	7.1	
24	8.8	6.1	8.2	7.56	
25	6.95	10.5	7.2	8.15	
25	1.65	4.2	7.8	4.6	

that this material is oxygen (see isotope experiments). Nevertheless, the oxygen is certainly not "free" in any phase of this migration as shown by the lack of decomposition of $KClO_4$ in blank experiments. Only when the oxygen becomes bound to a new atom (i.e. in CO_2) does the path of migration open up involving possibly a transfer from one crystal site to the other, without actual liberation of oxygen atoms or molecules. Thus, the essentially heterogenous and solid-solid character of the oxidation process is preserved, even though there is a "flow" of oxygen in the reacting system.

Oxidation of synthetic graphite in "mixed sandwich" tablets

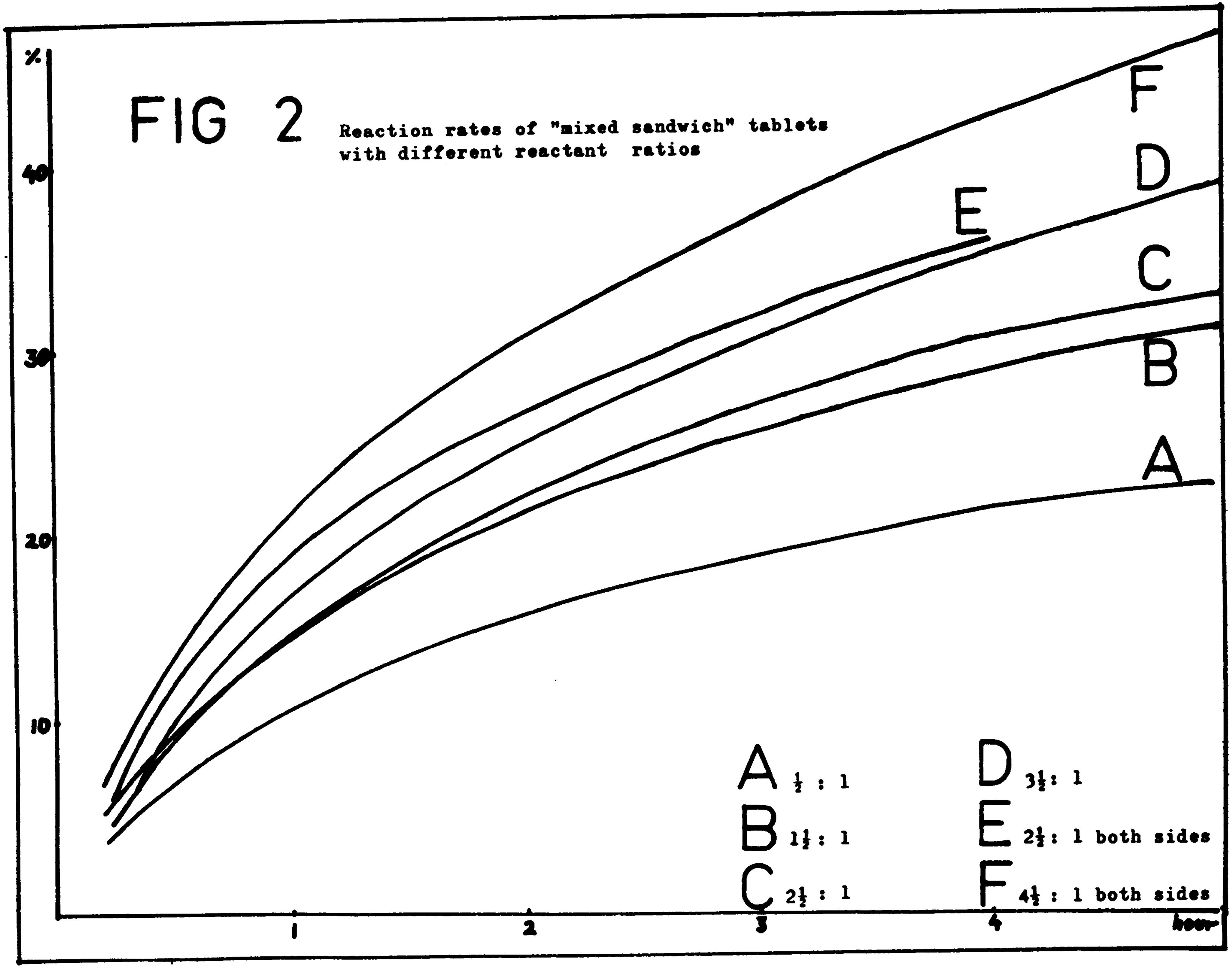
In this series of experiments, one milimole (12 mg) of graphite was mixed with ½ equivalent (36mg) of $KClO_4$ containing 3% of V_2O_5, and one or more additional $KClO_4/V_2O_5$ layer were pressed onte the mixed graphite/$KClO_4/V_2O_5$ layers. The Results are given in Table 8 and Fig.2. The points on curves and data in Table 8 are the average of at least 4 separate runs.

Table 8

Reaction of "mixed-sandwich" tablets at 380°. Data given for percentage oxidation of graphite.

Symbol	equivalent ratio $KClO_4$:C	percentage of reaction						$V_{in} = \frac{x}{t}$ $\frac{\%}{hour}$
		1/4 hr	½ hr	1 hr	2 hrs	4 hrs	5 hrs	initial rate
48 ▨	½ : 1	4.6	7	11	16	21.5	23	15.5
72 ☐ 48 ▨	1½: 1	5	9.5	15	21	29	31.5	18.5
144 ☐ 48 ▨	2½: 1	4.5	8.5	15	22	31	33	18
72 ☐ 72 ☐ 72 ☐ 48 ▨	3½: 1	6	10	16.5	25	35	39	21.5
72 ☐ 48 ▨ 72 ☐	2½: 1	6.2	11.8	19.4	27	36.2		23
144 ☐ 48 ▨ 144 ☐	4½: 1	7	13.5	22	31	43	47.5	27

FIG 2



Reaction rates of "mixed sandwich" tablets with different reactant ratios

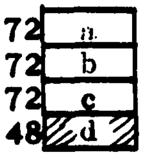
From Table 8 it is seen that the major part of the reaction is between the graphite and the oxidant mixed with it in the same layer. The "external" oxidant layers contribute also to the reaction, and the absolute amount of $KClO_4$ present in the system influences the overall oxidation rates of graphite. Significantly, the influence of the additional ("external") oxidant becomes relatively larger in the later stages of the reaction and the divergence of the reaction curves is more pronounced (see Fig.2). Again, the external "reservoir" of oxidant seems to make a flow of oxygen towards the reaction sites possible.

Three distinctly different groups of curves are evident in Table 8 and Fig. 2. The first one is the curve of the mixed graphite/$KClO_4/V_2O_5$ layer alone. Addition from one side only of more $KClO_4/V_2O_5$ layers to this mixed layer results in definately enahnced reaction rates, but the difference between the influence of 72mg, 144mg or three layers of 72mg each are small. The rate enahncement caused by the addition of a second layer onto the other side of the mixed layer is again significant, but relatively small. The results of the chloride analysis of the four separate layers in five tablets each of the total ratio of 3½:1 are given in Table 9.

The same trend is seen here as in Table 7, but the results are more reproducible. Again, the distance of the external layers from the actual reaction sites seems to have very little influence

Table 9

Percentage decomposition (after 24 hours, at 380°C) of the $KClO_4$ present in various layers of a "mixed-sandwich" tablet, all in the presence of 3% V_2O_5

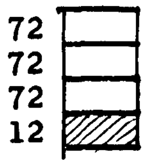
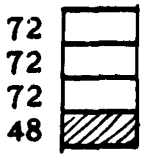
% decomposition of $KClO_4$				% decomp. of the three oxidant layers only	Symbol
$KClO_4/V_2O_5$ layers			$KClO_4/V_2O_5/C$ mixed layer		
a	b	c	d		
7.6	8.1	8.32	98.5	7.65	
7.4	6.95	8.85	93.8	7.45	
6.65	5.55	7.85	95	6.54	
6.62	5.48	6.28	95.5	6.27	
8.35	11	9.74	95.2	9.23	

on the percentage of decomposition of $KClO_4$. Table 10 below compares the results obtained in mixed tablets with the data of "sandwich tablets" with separate substrate and oxidant layers and also the data obtained in"mixed-sandwich" tablets.

Table 10 shows that the percentages of reaction, caused by the pure oxidant/catalyst layers are nearly the same irrespectively whether the graphite is a completely separate unmixed layer or contained in a mixed graphite/$KClO_4/V_2O_5$ layer. On the other hand, the percent reaction caused by the oxidant which was mixed with the graphite in

Table 10

The origin of the oxygen used up in the overall reaction

Run No.	time, hours	Symbol	% reaction* of graphite (sum A+B)	% decomp. of $KClO_4$ in the mixed layer	A**	B***
V_3	26	48 ▨	33.3	66.6	(33.3)	-
V_4	26	mixed $KClO_4$/ V_2O_5/C, ½:1	33.6	67.2	(33.6)	-
S_{39}	26.5		14.9	-	-	(14.9)
S_{40}	26.5		19	-	-	(19)
S_{41}	24	pure graphite	21.3	-	-	(21.3)
S_{42}	24		22.7	-	-	(22.7)
S_{43}	25		24.5	-	-	(24.5)
S_{44}	25		13.8	-	-	(13.8)
V_{21}	24		72	98.5	49.3	22.7
V_{22}	24		66.6	93.8	46.9	19.7
V_{23}	24	mixed graphite/ $KClO_4/V_2O_5$	64.1	95	47.7	16.6
V_{24}	24		60.2	95.5	47.8	12.5
V_{25}	24		74.5	95.2	47.6	26.9

* All the reaction percentages are taken on the basis of chloride analyses.

** A = % reaction of graphite with oxygen originating from the $KClO_4$ in the mixed layer

*** B = % reaction of graphite with oxygen originating from the $KClO_4$ in the external layers.

one of the layers of the sandwich tablets, was larger by a factor of about 1.5 than the percentage reaction obtained in the same time in a mixed, one layer grahpite/$KClO_4$/V_2O_5 tablet.

At present we are unable to offer any reasonable explanation for this experimental fact. Even the assumption of the flow of oxygen into the direction of the reaction-sites does not help in this case, as the net result of this would be more reaction in the remote $KClO_4$ layers but not in the mixture itself. In what manner the presence of adjoining $KClO_4$/V_2O_5 layers or even the oxygen flow is able to influence and enahnce the reaction in the graphite/$KClO_4$/V_2O_5 layer, is indeed very hard to rationalize. We believe that much more experimental data should be gathered before such an explanation is attempted.

<u>Experiments with Cl^{36} labelled $KClO_4$</u>

At various stages of the present research project the question arose, in the form of what species does the oxygen transport within the tablets take place. Clearly, the transport was a diffusion within the solid crystaline matrix and <u>not</u> a decomposition of the $KClO_4$ to KCl and gaseous O_2 followed by oxidation of the substrate by free oxygen (1). The movement of the oxygen in the crystalline lattice could conceivably take place in the form of ClO_4^- ions, or other less stable ions such as ClO_2^- or ClO^- or also in the form of $O_2^=$ or O^- ions. The appearance of O atoms or molecules was eliminated by the fact that at the reaction temperatures employed, even under the best vacuuum available, the evolution of gaseous oxygen was not measurable even after very extended periods.

A partial solution of this problem was obtained by performing some experiments with Cl^{36} labelled $KClO_4$ as the oxidant. A multilayer tablet was prepared, consisting of one layer of a mixture of graphite/$KClO_4$/V_2O_5, onto which two layers each of 72 mg unlabelled $KClO_4$/V_2O_5 were pressed and finally a layer consisting of 72 mg of labelled $KCl^{36}O_4$/V_2O_5. The whole tablet was allowed to react for 24 hours at 380°, and after this each layer was analysed separately for chloride contents and for radioactivity. The radioactivity of the layers within the experimental error was identical to the activity obtained in a similar multilayer tablet without the reaction period. This experiment proves conclusively, that no migration of any chlorine containing species occurs during the reaction, and therefore material transport does not involve either ClO_4^- or ClO_2^- or any similar chlorine containing ions.

The only reasonable remaining alternative is then material transport of oxygen towards the direction of the reaction sites involving movement of a species consisting only of oxygen atoms (charged or uncharged). Since liberation of free O atoms, or O_2 molecules was eliminated above, we believe that the oxygen transport involves migration of oxygen from one ClO_4^- ion to a neighbouring one, involving possibly defects in the crystalline structure of the substrate. This process must take place in a manner in which the oxygen atoms involved are always bound to at least one Cl atom and to two Cl atoms in the state of transition from one site to the other. The process is originated by the "memory" lattice of the KCl at the reaction sites which attract oxygen atoms from the neighbouring sites in the crystal.

B. Oxidation of high-melting organic compounds in solid-solid reactions.

In this part of our research project we investigated the solid-solid oxidation of three high melting organic substances, 1,1,2,2-tetraphenyl-1,2-bis (9,10 dihydroanthracenyl-9) ethane (TPDAE)(17), 9,9'-Bianthryl (18) and Anthracene. The oxidants employed were $KClO_4$ and mainly $KClO_3$ both in the absence and presence of catalysts. The most efficient among the latter proved to be again V_2O_5.

Comparatively low reaction temperatures could be employed; about 250-300° in the absence of catalysts and below 200° in their presence. All experiments were carried out in evacuated sealed pyrex-glass tubes. The tablets were as a rule pressed from well powdered, mixed reactants (-200 mesh) pressed in a Carver press under 6000 psi. In some experiments tablets of special shapes were employed, such as "sandwich" tablets, and also tablets in which the core was pressed from one of the reactants and covered by an outer layer of the second reactant. The diameter of the tablets was either 6 or 10 mm. The amount of oxidant was 25-200 mg and that of the substrate similar. When catalysts were used, they were admixed to the oxidant (about 2-5% w/w of the oxidant).

The tablets were dried at 100°C and afterwards in vacuo in the tubes in which they were subsequently heated.

The standard reaction time was 24 hours. After this, the tubes were cooled, opened and analysed. Constant care was taken as long as the tubes were sealed and especially during the heating period, that any accidental explosion (due to overheating or impurities) should not cause harm to the personnel (goggles, face masks and table shields). The reacted samples were worked up as follows: The inorganic material was dissolved in water, and analysed for chloride contents by a "Radiometer" automatic titrator. From the results of this analysis the percentage decomposition of the $KClO_4$ or $KClO_3$ was calculated. The organic material was dissolved in ether and if possible purified according to accepted procedures. Identification of the organic product was carried out also by determining the UV and IR spectra of various fractions. Reproducibility of the experiments in most cases was satisfactory.

Blank experiments with the oxidants alone or with oxidant/catalyst mixtures showed that at the reaction temperature employed less than 1% decomposition took place during 24 hours.

In many cases, especially when the main organic product was anthraquinone, a part of this sublimed and was deposited on the walls of the tube in the form of long needles.

In some experiments with bianthryl, no reaction took place at 235°C. It was found, that in these, the substrate used was not sufficiently purified and contained some metallic Sn or Sn-salts remaining from the synthetic procedure. After more careful purification, the results shown in Table 13 were obtained.

Table 11

Experiments with TPDAE (1,1,2,2,tetraphenyl,-1,2-bis (9,10-dihydroanthracenyl-9) ethane), heating period of 24 hours. All the tablets were composed of mixed reactants

Amount of TPDAE mg	oxidant (mg)	additive	T°C	% decomp. oxidant	Remarks
50	$KClO_4$ 50	-	260	4	no product isolated
14	$KClO_3$ 100	-	285	23	Anthraquinone (m.p. 280°) isolated by sublimation and identified
14	" 196	-	285	20	
50	" 50	-	285	40	
25	" 25	-	285	41	
50	" 50	-	260	36	
50	" 50	-	235	21	
50	$KClO_4$ 50	$Fe_2(SO_4)_3$ 5%	235	4.2	No product isolated
25	$KClO_3$ 25	V_2O_5 5%	310	?	sample exploded
25	" 25	" 2%	310	?	" "
25	$KClO_4$ 25	" 5%	310	14	Anthraquinone
16.5	" 33.5	" 5%	310	13.7	isolated
25	" 25	" 2%	310	9.1	" "
16.5	" 33.5	" 2%	310	9.6	" "
25	$KClO_3$ 25	V_2O_5 5%	285	?	sample exploded
25	" 25	" 2%	285	?	" "
25	$KClO_4$ 25	" 5%	285	9.7	Anthraquinone
16.5	" 33.5	" 5%	285	9.7	isolated
25	" 25	" 2%	285	7.5	" "
16.5	" 33.5	" 2%	285	7.3	" "

Table 11 (cont.)

Amount of TPDAE mg	oxidant (mg)		additive		T°C	% decomp. oxidant	Remarks
25	$KClO_3$	25	V_2O_5	5%	260	?	sample exploded
25	"	25	"	2%	260	?	" "
25	$KClO_4$	25	"	5%	260	3.9	only chloride analysis performed, no organic product identified
16.5	"	33.5	"	5%	260	4	
25	"	25	"	2%	260	4.1	
16.5	"	33.5	"	2%	260	4	
25	$KClO_3$	25	V_2O_5	5%	235	?	strong charring
25	"	25	"	2%	235	?	" "
25	$KClO_4$	25	"	5%	235	2	chloride analysis only
25	"	25	"	2%	235	2	" " "
25	$KClO_3$	25	V_2O_5	5%	210	?	strong charring
25	"	25	"	2%	210	?	" "
25	$KClO_4$	25	"	5%	210	1	chloride analysis only
25	"	25	"	2%	210	1	" " "
25	$KClO_3$	25	V_2O_5	5%	185	86.2	isolated 50% of anthraquinone, yield based on TPDAE actual yield probably considerably larger owing to difficulties in purification procedure
25	"	25	"	2%	185	90.6	
25	$KClO_3$	25	V_2O_5	5%	160	0.8	chloride analysis only
25	"	25	"	2%	160	1.3	" " "

Table 12

Oxidation of TPDAE by $KClO_3$ in sandwich tablets at 185°C during 24 hours

symbols used for composition of layers:

$\boxed{A}$ = TPDAE
$\boxed{B}$ = $KClO_3$
$\boxed{C}$ = V_2O_5
$\boxed{D}$ = $KClO_3/V_2O_5$
$\boxed{E}$ = $TPDAE/V_2O_5$
$\boxed{F}$ = KCl

TPDAE mg	$KClO_3$ mg	additive		Nature of tablet and symbol		% decomp. oxidant	Remarks
25	25	V_2O_5	5%	$\boxed{A}$ $\boxed{D}$	sandwich 2 layers	88%	Anthraquinone identified
50	50	"	5%	"	"	85%	" "
25	2x12.5	"	5%	$\boxed{D}$ $\boxed{A}$ $\boxed{D}$	sandwich 3 layers	90%	" "
50	2x25	"	5%	"	"	83%	" "
25	25	V_2O_5 KCl 25 mg	5%	$\boxed{A}$ $\boxed{F}$ $\boxed{D}$	sandwich 3 layers	39%	" "
25	25	V_2O_5 KCl 12.5mg	5%	"	"	54%	" "
50	2x25	V_2O_5, KCl 2x25mg	5%	$\boxed{D}$ $\boxed{F}$ $\boxed{A}$ $\boxed{F}$ $\boxed{D}$	sandwich 5 layers	60%	" "
25	25	V_2O_5	5%	$\boxed{E}$ $\boxed{B}$	sandwich 2 layers	4%	No product identified
25	25	V_2O_5	25 mg	$\boxed{A}$ $\boxed{C}$ $\boxed{B}$	sandwich 3 layers	7.3%	Only chloride analysed
12.5	12.5	"	12.5mg	"	"	6.5%	" "
50	200	V_2O_5	5%	$\boxed{D\ \boxed{A}}$		96%	Organic layer strongly charred
200	50	"	5%	$\boxed{A\ \boxed{D}}$		57%	Anthraquinone identified

Table 13

Oxidation of 9,9'-Bianthryl by $KClO_3$ containing 5%(w/w) of V_2O_5 heating period of 24 hours.

Symbols for the composition of layers

$\boxed{A}$ = Bianthryl $\boxed{B}$ = $KClO_3/V_2O_5$ 5% (w/w)

amount of Bianthryl mg	amount of $KClO_3/V_2O_5$ mg	T°C	Nature of tablet or symbol	% decomp. oxidant	Remarks
25	25	235	mixed, one layer	?	Sample exploded
25	25	210	"	?	" "
25	25	185	"	81	Anthraquinone identified
25	25	185	"	86	
50	50	185	"	76	" "
50	50	185	sandwich 2 layers $\begin{array}{\|c\|}\hline A\\\hline B\\\hline\end{array}$	83	" "
100	100	185	" "	70	" "
100	2x50	185	sandwich 3 layers $\begin{array}{\|c\|}\hline B\\\hline A\\\hline B\\\hline\end{array}$	89	" "

Table 14

Experiments with Anthrocene, heating period Of 24 hours

Symbols for the composition of layers

A = Anthracene

B = $KClO_3$

C = $KClO_3/V_2O_5$ 5%

D = KCl

amount of Anthracene mg	amount of $KClO_3$ mg	additive	T°C	Nature of tablets or symbol	% decomp. of oxidant	Remarks
50	-	-	160		-	No sublimation occurred
50	50	-	160	mixed, 1 layer	2.4	
50	50	-	160	sandwich 2 layers A B	2.1	
50	50	V_2O_5 5% of oxidant	160	mixed, 1 layer	81	Anthraquinone identified
50	50	" 5%	160	sandwich 2 layers A C	24	"
2x25	50	" 5%	160	sandwich 3 layers A C A	40	"
50	2x25	" 5%	160	" C A C	80	"
50	50	" 5% +25mg KCl	160	" A D C	25	"
50	50	V_2O_5 5% of oxidant + 50mg KCl	160	" "	1.1	-
25	25	V_2O_5 5% of oxidant	135	mixed, 1 layer	58	Antrhaquinone identified
50	50	"	135	" "	52	"
50	50	"	135	sandwich 2 layers A C	32	"
100	2x50	"	135	sandwich 3 layers C A C	21	"
25	25	"	110	mixed, 1 layer	10.7	"
25	25	"	110	sandwich 2 layers A C	6	"

The results in Tables 11-14 show that the solid-solid oxidation of well defined organic molecules like anthracene, bianthryl or TPDAE has features very similar to the oxidation of various forms of carbon or cross-linked high-polymers. The same type of catalysts are again effective (i.e., V_2O_5, $Fe_2(SO_4)_3$). As we were interested to work at relatively low reaction temperature, most experiments were carried out with $KClO_3$ rather than with $KClO_4$, as the former was effective at lower temperatures, where almost no charring or other decomposition of the substrate occurred. The temperature range which can be used is rather narrow. E.g. with TPDAE/$KClO_3$/V_2O_5 mixed tablets, explosion or very strong charring occurred above 210°, while relatively high yields in a controlled oxidation process were obtained at 185°C, but lowering the temperature a further 25°C to 160°C, stopped the reaction completely.

Accordingly, the experiments with "sandwich tablets" (see Table 12) of TPDAE/$KClO_3$ were all performed at 185°C. Obviously, the 24 hour reaction period was more than necessary, as shown by the practically identical percentages of decomposition of $KClO_3$ in mixed and in sandwich tablets containing the same amounts of the reactants, when the catalyst (V_2O_5) was mixed with the oxidant. On the other hand, when the catalyst was contained only in the substrate layer, practically no reaction took place.

KCl inhibits the reaction only slightly. In sandwich tablets in which a KCl layer was pressed between the substrate layer and the oxidant layer, 12.5 mg of KCl allowed still 54% reaction to take place, and even a dividing layer of 25 mg KCl (about equal in bulk to that of the oxidant layer above it) still permitted a reaction of 39% in 24 hours. With the same arrangement on both sides of the substrate layer, i.e., in a five layer tablet $KClO_3$//KCl//TPDAE//KCl//$KClO_3$, the decomposition percentage was even higher (i.e. 60%).

This seems to hint to a possibility of oxygen transfer even through a normal KCl crystal lattice, even though the material transfer through the previously postulated memory lattice may be more efficient and rapid.

The efficiency of the catalyst fell considerably when interposed between the substrate and the oxidant. In such experiments ($KClO_3$//V_2O_5//TPDAE) the oxidation percentage in 24 hours was only about 7%. This fact seems to show that the role of the catalyst is more important in the transfer of oxygen from one site in the oxidant to another, than in the actual transfer of oxygen from the oxidant to the substrate at the boundary layer of these two.

Two special tablets were prepared. In the first, the substrate tablet prepared separately, was completely enveloped in a layer of a mixture of $KClO_3/V_2O_5$. Under these circumstances the oxidant decomposed almost completely in 24 hours, but at the same time the substrate gave much carbonaceous material, from which anthraquinone could not be isolated. On the other hand, when the oxidant/catalyst mixture was enveloped in a layer of the substrate, the percentage decomposition of $KClO_3$ was only 57% but the substrate remained uncharred and anthraquinone could be isolated and identified.

Apart from the anthraquinone which could be generally easily separated by sublimation, the organic product contained also a fraction which gave UV and IR spectra rather similar to benzophenone (the expted second product of oxidation of TPDAE) but the material was contaminated and we did not succeed in purifying it completely. Some of the above described experiments were repeated using 9,9'-bianthryl as the substrate and $KClO_3/V_2O_5$ as the oxidant (Table 13). In all cases, the results were identical with those in Tables 11 and 12, even as to the dependence on the reaction temperature.

Experiments with anthracene as the substrate and $KClO_3/V_2O_5$ as the oxidant (Table 14) showed that in this system even lower reaction temperatures can be employed. At 135°C reaction percentage were still reasonably high, and even as low as 110°C reaction could be well verified both in mixed and in sandwich tablets.

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