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Solid State Chemical Reactions (with special reference to the kinetics of the reaction of inorganic oxidants with poly-divinylbenzene).

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EXPERIMENTAL

Abstract

The heterogeneous reaction in the solid phase of various high melting organic substances with solid oxidants in the presence of catalysts was investigated. Oxidants used were potassium perchlorate, potassium bromate, potassium nitrate, potassium chlorate, potassium iodate, chloranil and selenium dioxide. The substrates used were polycyclic aromatic compounds and polymers, in particular a co-polymer of p-divinylbenzene and p-ethylstyrene. A large number of high-melting substances, e.g. inorganic salts, oxides and metal powders were tried as catalysts for the reaction.

It was found that as a rule Lewis acids ($Al_2(SO_4)_3$, $Fe\,Cl_2$, etc.) catalyzed the reaction while basic substances (Na_2CO_3, LiOH, etc.) inhibited it.

The empirical equation

$$dx/dt = k\,(a-x)/x^{2/3}$$

was found to fit the kinetic curves for the catalyzed $KClO_4$, KIO_3 and $KBrO_3$ oxidations of pDVB and the zero order equation

$$dx/dt = k$$

was found to fit the kinetic data for the catalyzed $KClO_3$ oxidation of pDVB.

INTRODUCTION

(a) Solid State Reactions in General

Reactions in the solid phase were first observed by Faraday and Stodart(7) in the diffusion in metals at high temperatures and by Spring(56) in the reactions between inorganic solids. The first extensive studies of reactions in the solid state were by Tammann(9, 57, 58) whose concept of the mechanism involved was a diffusion occurring by "Platzwechsel" of the atoms. He proposed that the minimum temperatures at which this exchange took place were 0.3Ts for metals, 0.5Ts for oxides, salts and some silicates and as high as 0.9Ts for some organic molecules, where Ts is the melting point in $^{\circ}$K.

In the past 50 years intensive investigations have been carried out in the solid state as evidenced by the monographs of Hedvall(24) and Garner(11).

It is generally accepted that solidstate reactions do occur but some workers have disputed that the mechanism of the reaction is directly between solids. Ginstling et al(14, 15, 47, 48, 49) hold the viewpoint that solid state reactions between powdered solids are unlikely processes except at very high temperatures since the contact area between the particles presents too small a cross-section for rapid diffusion. They claim that these so-called solid reactions occur by a vaporization mechanism.

Borchardt$^{(2)}$ developed criteria whereby it is possible to determine definitely when a vaporization method cannot be the principal mode of mass transport so that Ginstling's generalization for these powder reactions is questionable. Ginstling and co-workers based their conclusions on experiments in which the conditions were changed from those of the workers who proposed a solid state mechanism for the same reactions. Borchardt found that for U_3O_8–metal mixtures, the dissociation temperature for U_3O_8 was much higher than the temperatures used in the reactions. Thus if the only alternative mechanism involves solid state diffusion processes then it would follow that the reactions are truly in the solid state.

The classical studies of reactions in the solid state by Tammann (loc. sit) treated on the equilibrium conditions involved. The basic tenet was that reactions in the solid state proceed exothermically until a considerable fraction of the reactants is consumed. Complete reaction is difficult to achieve, usually, because of the barrier of the product layer between the reactants. Thus, except for cases of miscibilityof reactants and product phases, equilibrium is usually not possible in reactions in the solid state.

Tammann postulated that a product layer is formed during most solid-solid reactions having a rate of growth $dl/dt = b/t$

where l is the thickness of the product layer,

t is the heating time

and b a temperature-dependent factor.

Jander(29) developed this relationship a step further, giving the reaction rate in terms of rate of growth of the product layer, or

$$dy/dt = k/y$$

where y is the thickness of the product layer between the two reactants.

The equation in its integrated form is $y^2 = 2kt$.

Jander further treated on the processes of diffusion in solid state reactions when the reacting systems consist in mixtures of fine powders containing one of the reactants in large excess and proposed a relationship whereby the rate constant of a reaction is given by:

$$\left(1 - \sqrt[3]{1 - \alpha}\right)^2 = \frac{C}{R^2}\, t = C''t$$

where α = fraction of completion of reaction

and R = grain radius of the minor component assumed to be monodisperse and completely surrounded by the excess reactant.

The rate constants determined by these or other equations are more or less structure-sensitive and cannot be employed directly to establish a reaction mechanism for two particular reasons. One, the phase boundary processes are complex and irreproducible, and two, the participating phases are usually not in equilibrium internally. The state of solid surfaces and the degree of contact between them are so irreproducible and vague that the phase boundary processes cannot be controlled. The lack of internal equilibrium is due to lattice disturbances and the energy required for their motion is lower than the migration energy of particles in equilibrium.

The kinetics of solid state reactions will depend on the diffusion of the components and will be affected by either of two possibilities:

(a) The processes occurring at the phase boundaries are infinitely rapid compared with the diffusion velocity and equilibrium is constantly established at the boundaries so that the diffusion in the product layer is rate-determining.

(b) The processes occurring at the phase boundaries are <u>not</u> infinitely rapid compared with the diffusion velocity so that both the diffusion and the boundary processes are rate-determining.

Reaction mechanisms are discussed, for the above reasons, for solids internally in equilibrium and the theories applied thereafter to the reactions of non-equilibrium solids. The mechanisms obtained offer a qualitative basis for the understanding of reactions of non-equilibrium solids (Cohn(3)).

Mechanisms of reactions in the solid state have been studied extensively by Tammann, by Hedvall(24), by Jander(29, 30), by Jost(31) and by Wagner(62). In general these reactions are interpreted as occurring by the movement of ions and electrons. The influence of disorder and dislocation is very greatly stressed.

(b) The decomposition and reactions of perchlorates and allied substances in the solid phase

The first investigations of the reactions and decompositions of perchlorates and other oxygen rich substances by Heinrich(26), Crespi and Caamano(4), Heertjes and Houtmann(25), Elliott(6), Spice and Staveley(55), Hofmann and Marin(28), Schneider(52), Otto and Fry(37), Kendall and Fuchs(32), Marvin and Woolaver(36), Taradoire(59), were mainly observations of the decomposition points of the various substances, their behavior in the presence of combustible substances and the effect of foreign ions on the decompositions.

The first fully detailed studies of the decomposition of perchlorates and allied substances, including kinetics of the decomposition were by Glasner and Simchen(16, 17), Glasner and Weidenfeld(18) and Bircumshaw and Phillips(1).

Bircumshaw and Phillips found the critical influence of impurities, especially KCl, in the decomposition of $KClO_4$. They state that the usual theories derived for chemical reactions involving solid decompositions are inapplicable at the high temperatures which lead to a molten system and considerable variation of experimental results. The researches of Glasner and Simchen and of Glasner and Weidenfeld along the same lines find more or less the same effects due to KCl and propose an equation similar to that of Prout and Tompkins(50). The Prout and Tompkins equation, for the decomposition of $KMnO_4$ crystals, is a modified auto-catalytic expression

$$dx/dt = kx/a(a-x)$$

Glasner and Weidenfeld propose that in the decomposition of potassium chlorate, potassium perchlorate is formed by transfer of atomic oxygen from the chlorate ion to a chloride ion. Vanden Bosch and Aten(61), by labelling isotopically the oxygen of chlorate found that this did not occur.

In the decomposition of potassium perchlorate, Harvey et al(20, 21) found that chlorate was formed as an intermediate which then decomposes to chloride. The decomposition of perchlorate is the rate-determining step as shown by the fact that the concentration of chlorate remains low.

In these laboratories the reaction of $KClO_4$, $KClO_3$ and KNO_3 with various combustible substances, with and without catalysts has been studied by Patai and co-workers(39-46). Various mathematical relationships were proposed and various mechanisms were postulated. In the reaction between potassium perchlorate and carbon the empirical rate equation

$$dx/dt = k\ (a-x)^{2/3}\ /x^{1/3}$$

was proposed(44). The reaction rate was found to be influenced by the initial ratio of the reactants, the amount of potassium chloride formed and the radius of the perchlorate particles. Patai and Rajbenbach(42) investigated the effects of various catalysts on the same solid-solid reactions and found that the kinetics followed the Tammann equation $dy/dt = k/y$. The mode of action of the catalysts was interpreted as being due either to their migration into the reacting substances with consequent weakening of the valence bonds of the reacting atoms (paralleling the effect of catalysts on the thermal decomposition of solids) or to their participation in the transition complex of the two reactants with consequent lowering of energy of activation of the complex-formation or due to an oxygen-carrying role.

Fukushima and Horibe(8) investigated the mechanism of the catalytic action of manganese dioxide on the decomposition of potassium chlorate using heavy oxygen as an isotopic tracer. They concluded that an unstable intermediate compound is formed between $KClO_3$ and MnO_2 and that gaseous O is evolved by the decomposition of this intermediate.

The influence of catalysts on solid-solid reactions is a very new field. Hedvall(23) points out the recent advances in the understanding of the nature of catalytic processes. Emphasis on the mobility of electrons at surfaces and the exchange of electrons at phase boundaries between catalyst and substrate has been made in the most recent researches. Such treatment of these processes is given by De Bruijn(5) for catalytic reactions on inhomogeneous surfaces and by Hauffe(22) in the role of various oxides and sulfides as heterogeneous catalysts.

RESULTS AND DISCUSSION

I. Preliminary Experiments

At the beginning of the work, experiments were carried out on solid-solid reactions between oxidants and various organic substrates, especially polycyclic compounds, in the presence and absence of catalysts with the view to finding whether reactions in the solid phase gave the same products as in a homogeneous reaction in solution. The number of substrates was very limited because only a few such organic compounds remain solid and do not undergo thermal decomposition at the high temperatures necessary for the reactions.

These first reactions were studied qualitatively and the work on them was not extended. It was seen that the products of the reaction were such as to complicate any kinetic study unduly.

Preliminary reactions between $KClO_4$ and various polymers showed that a suitably high melting polymer would be the ideal substrate for the present study since the course of the reaction would be most likely

$$\text{solid} + \text{solid} \rightarrow \text{gas} + \text{solid}$$

and/or

$$\text{solid} + \text{solid} \rightarrow \text{solid} + \text{solid}$$

A kinetic study of such types of reactions would be feasible.

The main types of preliminary experiments carried out were as follows:

(a) Anthracene and selenium dioxide

These mixtures melted at less than 150° and in order to carry out the reactions in the solid phase they were heated at temperatures up to 120°C. From 100-120°C some high-melting material was formed, but could not be identified, owing to the difficulties of separation and the very small amount obtained. Most of the anthracene remained unchanged. The ultraviolet spectrum of the product indicated the presence of traces of anthraquinone.

(b) Chrysene and $KClO_4$.

There was no reaction of chrysene with $KClO_4$ either in the absence or in the presence of added substances (K_2CO_3, $Fe_2(SO_4)_3$ and LiCl) at 200°C. The starting materials were recovered unchanged.

(c) Sodium cyclohexylcarboxylate with $KClO_4$, KNO_3, SeO_2 and chloranil (tetrachlorobenzoquinone).

The products were studied spectrophotometrically. The U.V. spectrum revealed the formation of benzoic acid. In a typical experiment, a tablet containing about 650 mg of $KClO_4$, 300 mg of

$C_6H_{11}COONa$ and 30 mg of $Fe_2(SO_4)_3$ was heated at 320°C in a closed tube for 22 hours. Analyses for chloride showed that 23% of the perchlorate had reacted and about 60 mg of benzoic acid were obtained, identified by melting point, mixed melting point and U.V. spectrum. The tablet remained mechanically stable throughout the reaction and only a small amount of brown insoluble carbonaceous material was formed. At higher temperatures the mixtures reacted explosively (at 340°C in the presence of the above-stated amount of $Fe_2(SO_4)_3$ and at 360-370°C in the absence of catalyst). At 340°-350° up to 100% of the $KClO_4$ decomposed even in uncatalyzed reactions, after 20-24 hours, but the organic product was entirely a black carbonaceous material. At lower temperatures the reaction was slow but the presence of benzoic acid was revealed in the product by its U.V. spectrum.

Similar results were obtained from mixtures of KNO_3 and $C_6H_{11}COONa$ with $Fe_2(SO_4)_3$ at 225-300°C and also with mixtures of SeO_2 and $C_6H_{11}COONa$ at 200°C but in the latter case the mixture fused and the reaction probably took place in the molten phase.

Using chloranil (m.p. 290°) as the oxidant, with $C_6H_{11}COONa$ at 140-200°C (16-20 hours heating), 15-20% of benzoic acid were obtained.

[illegible]) Other substances: Oxamide and $KClO_4$ did not react at 300°C and gave only 1.2-1.6 % reaction (analysed for chloride) at 325° to 400°. Dicyclohexylamine hydrochloride with $KClO_4$ reacted explosively at 250° and decomposed completely at as low as 200-220°C. At lower temperatures (170-180°) the starting materials were recovered unchanged.

(e) Polymers: Various polymers were prepared with the view to finding a heat stable and high melting polymer suitable for reactions with various oxidants in the solid state. Polymers from indene, vinylnaphthalene, cinnamal fluorene, acenaphthene and acenaphthylene were prepared. Copolymers from vinylnaphthalene/divinylbenzene (DVB), styrene/DVB and acenaphthylene/DVB were also prepared. As none of these had a sufficiently high melting point for reaction with $KClO_4$ in the solid phase, it was decided to use a copolymer of 40 % DVB and 60 % p-ethylstyrene (henceforth called pDVB or polydivinylbenzene) and to investigate its oxidation in the presence of various catalysts. The remaining work was the study of this catalyzed reaction using $KClO_4$, $KClO_3$, $KBrO_3$ and KIO_3 as the oxidants and a large number of inorganic and organic substances of suitably high melting-points as the catalysts.

II. The Catalyzed Solid-Solid Reaction Between pDVB and Various Inorganic Oxidants

A. $KClO_4$ as Oxidant.

(a) Ignition Times and Temperatures

The various mixtures of $KClO_4$-pDVB-catalyst were heated at various temperatures until they ignited (see Experimental Part for details). The results are shown in Table 1, page 16, arranged in descending order of flammability. As a comparison is made with samples not containing an added substance, the table serves as an assessment of the relative catalytic activities of the added substances.

The table shows that most of the Cl^- and $SO_4^=$ salts used are catalysts, with the exceptions of NaCl, KCl, and possibly $PbCl_2$ and $PbSO_4$. KI appears higher in the table than other alkali metal halides. Otherwise there is agreement in the results for compounds of the same classes. Metal powders and basic substances inhibit the reaction. There appears to be an influence of both the cation and the anion in the effect of the added substances. Thus $PbCl_2$ and $PbSO_4$ are low in the table as compared with salts of other metals and KI is high while KBr is low. Similarly, among the metal powders Cu appears to be far less inhibitory than Zn or Al, and as the densities and the surface areas of the additives Cu and Zn are very similar the difference in their effects might depend on physical properties affecting the diffusion rate.

The effects of the added substances in the ignition tests are paralleled by the results for the same mixtures in kinetic runs at lower temperatures and in vacuum (see section (b) of Discussion of Results).

The time lag required for the temperatures of the samples to rise to the ignition temperatures was not taken into account in the figures presented in the table. This period will be approximately the same for samples of the same size and should be in the neighborhood of 12 seconds, the time required for ignition at very high temperatures, when samples ignite as soon as they reach the ignition temperature.

(b) Effects of added substances on the rate of reaction.

The effects of various catalysts are compared according to the rate constants of the reaction in Tables 2, 3, 4, 5, pages 20 - 23. Some of the typical results are represented in Figure 1, page 25. Table 2 shows that the oxides Fe_2O_3, Cr_2O_3 and MnO_2 either do not affect the rate or else lower the rate while V_2O_5, LiCl and $Fe_2(SO_4)_3$ catalyze the rate to more than eight times the uncatalyzed rate.

TABLE 1

Ignition Times at Various Temperatures

$KClO_4$ - pDVB - catalyst mixtures.

Time of Ignition (Seconds)

Sample No.	Catalyst	Temp. °C →	390	400	410	420	430	440	450	460	470	480	490	500	510	520	530
38	V_2O_5					57	46										
81,97,71	$Al_2(SO_4)_3$		∞	59 41	58	53	53	26	39	21							
79	CuCl					42		29		24							
88	$CoSO_4$							47		38		20		17			
74	$FeCl_2$							33	28			16	16	19	10		
55	KI								39	38		21	22				
112	$K_2Cr_2O_7$									50			17			12	
75	$MnSO_4$									36		27		19			
101	$MnCl_2$					76	53	42	45								
104	NH_4Cl					103	86	59	49								
58	LiCl					∞	100										
92	$NiSO_4$					121	90	70	50	48							
44	K_2CrO_4							131	98	66	45						
43	KNO_3						∞	119	106	76							

TABLE 1 (cont'd)

Sample No.	Catalyst	Temp. °C →	390	400	410	420	430	440	450	460	470	480	490	500	510	520	530
93	$ZnSO_4$								109		56		33		19		14
68	K_2CO_3										51	60	39				
56	Li_2SO_4										103	50	44				
73	NaI						194	112	80	79							
70	NaBr											57	54	39			
76	$PbCl_2$									90	88	70	46	39			
AK	None									115 115	80	75 75	57 58	42 42	42 34	33	26
54	KBr							∞		114		51		42			
82	NaCl								196			73	59	55			
89	$PbSO_4$									112	107	65	47	54			
57	KCl													58 35			
53	Cu									∞		108	76	57			
69	Na_2CO_3									89	58	60	51				
52	Fe									130	76	61	48				
34	Al											84	57				
108	Fe										105	96	62				
103	Sb_2O_5									134		113	81				
78	Pb_3O_4								∞				165	84			

TABLE 1 (cont'd)

Sample No.	Catalyst	Temp. °C →	390	400	410	420	430	440	450	460	470	480	490	500	510	520	530
110	Al									∞	∞	162	115	94	64	52	44
67	$CaCO_3$										∞		82	105			
90	Li_2CO_3									∞			245	105 106	81	56 39 30	
50	Zn										∞		283				

Table 3 shows the effect of some of the above and of other added substances at a higher temperature. Again, V_2O_5, LiCl and $Fe_2(SO_4)_3$ and also Al powder strongly catalyze. The oxides MgO and Cr_2O_3 strongly inhibited the reaction. K_2CO_3 inhibited the reaction to about one-half the rate for the $KClO_4$-pDVB reaction.

Table 4 shows the effect of two of the catalysts in the same ratio to $KClO_4$ as above but with the $KClO_4$ and pDVB in equal proportions by weight. There is about the same degree of catalysis but with high proportions of pDVB the tablets were mechanically less stable and reproducibility was poor.

Table 5 represents the main body of work done in this section, wherein a ratio of 5 parts $KClO_4$ per part of pDVB by weight and a ratio of 0.028 parts catalyst per part $KClO_4$ by weight and a temperature of 350°C were used throughout. The catalysts mentioned above were used again and others chosen to illustrate certain trends previously observed.

It is evident that more than one factor is involved in the catalytic mechanism (see section E).

It can be seen that catalysis is strong with substances likely to be proton donors, e.g. strongly ionic compounds or acid compounds (Lewis acids) such as $Al_2(SO_4)_3$, $Fe_2(SO_4)_3$, LiCl, NH_4Cl, etc., whereas inhibition occurs with proton acceptors, e.g. basic compounds, such as K_2CO_3, Na_2CO_3, LiOH, Li_2CO_3. For example, the rate constant with the latter two substances was one-thirtieth of the uncatalysed rate.

Metals did not show any appreciable activity as catalysts while they are renowned for their effect in gas phase reactions at high temperatures. In the present reactions they behaved more or less as inert substances, at times even inhibiting the reaction.

Of the oxides, only vanadium pentoxide showed any catalytic activity. All others used showed a mild to strong inhibition.

Apart from Lewis acids actual protonic acids, for example, molybdic acid, dicyclohexylamine hydrochloride and phosphoric acid, were used also and were found to catalyze the reaction between $KClO_4$ and pDVB.

Phosphoric acid at a concentration of 0.01 ml per pellet of 250 mg at 350°C only slightly catalyzed the reaction but at 400°C and with 0.05 ml H_3PO_4 per pellet the reaction proceeded explosively.

Experiments with boric acid at 400° gave only mild catalysis in some cases, while in others explosion occurred. It is evident that the temperature sensitivity of these reactions was very large and the differing behaviour must be due to slight fluctuations of the furnace temperature.

An anion and a cation exchange resin (Amberlite IR 410, quaternary amine type and Amberlite IR 120, sulfonic acid type, respectively) were used as catalysts under the same conditions. The cation exchanger catalyzed the reaction to six times the uncatalyzed rate and the anion exchanger to about three times the uncatalyzed rate. This was the only instance of a basic substance having a catalytic effect. In view of the complicated structure of such a resin we cannot put forward an explanation.

(c) The Empirical Rate Law of the $KClO_4$-pDVB Reaction and of the Catalyzed $KClO_4$-pDVB Reaction.

It is logical to assume that in the solid-solid reaction between $KClO_4$ and pDVB the main rate-determining factor will be the behaviour of the $KClO_4$ particle since pDVB is a rigid, cross-linked, non-ionic solid having very slight or no mobility. Furthermore, experiments were carried out at temperatures far below the melting point of the polymer and considerably above the Tammann temperature of $KClO_4$.

The only other factor involved in the $KClO_4$-pDVB reaction would be the influence of the products of the reaction on the ensuing reaction.

TABLE 2

Effects of Catalysts

$KClO_4$:pDVB = 2.5:1 (w/w) @ 350°C

Catalyst:$KClO_4$ = 0.028:1 (w/w)

Run No.	Catalyst	k (hr^{-1}) (Eq.V, p.27)
E	V_2O_5 (0.14:1)	0.868
M-2	LiCl	0.734
47	$Fe_2(SO_4)_3$	0.656
F, G	V_2O_5	0.575, 0.448
31	None	0.063
Z	Fe_2O_3	0.063
30	Cr_2O_3	0.031
Y	MnO_2	0.003

TABLE 3

Effects of Catalysts

$KClO_4$:pDVB = 2.5:1 (w/w) @ 400°C

Run No.	Catalyst (% in mixture)		k (hr^{-1})
C	V_2O_5	10%	samples exploded
M	LiCl	2%	2.8
R	$Fe_2(SO_4)_3$	0.2%	0.96
L	Al	2%	0.74
P	Al	0.5%	0.56
K	None		0.46
D	K_2CO_3	10%	0.336
I	K_2CO_3	2%	0.232
A	Cr_2O_3	10%	0.132
B	MgO	10%	0.008

TABLE 4

Effects of Catalysts

$KClO_4$:pDVB = 1:1 (w/w) @ 350°C
catalyst:$KClO_4$ = 0.028:1 (w/w)

Run No.	Catalyst	k (hr^{-1})
V,W,45	$Fe_2(SO_4)_3$	0.985
U,46	V_2O_5	0.24, 0.179
X	None	0.077

TABLE 5

Effects of Catalysts

$KClO_4$:pDVB = 5:1 (w/w) @ 350°C
catalyst:$KClO_4$ = 0.028:1 (w/w)

Run No.	Catalyst	k (hr^{-1})
187	Amberlite IR 120	0.412
77	Ferric Ammonium Sulfate	0.39
32,42	$Fe_2(SO_4)_3$	0.35, 0.35
58,83,84	LiCl	0.27 (ave.)
81,71,97	$Al_2(SO_4)_3$	0.079, 0.262, 0.250
188	IR 410	0.219
38,33	V_2O_5	0.179, 0.080
94,95	$FeCl_2$	0.152
185	H_2MoO_3	0.139
125	Dicyclohexylamine hydrochloride	0.122
66	K_2SO_4	0.10
75	$MnSO_4 \cdot H_2O$	0.098
104	NH_4Cl	0.091
76	$PbCl_2$	0.088
64	$CaSO_4$	0.084

TABLE 5 (cont'd)

Run No.	Catalyst	k (hr^{-1})
65	Na_2SO_4	0.084
80,98	$CuCl_2$	0.091, 0.067
87	NH_4Br	0.079
92	$NiSO_4 \cdot 6H_2O$	0.079
52,108	Fe	0.070, 0.051
184	H_3PO_4 (0.01ml/pellet)	0.065
39,40	None	0.060, 0.056
54A,54B	KBr	0.057, 0.053
55A,55B	KI	0.057, 0.053
57A,57B	KCl	0.057, 0.053
85,101	$MnCl_2$	0.057, 0.054
72	$BaSO_4$	0.056
88,96	$CoSO_4$	0.054, 0.052
82,99,100	NaCl	0.047, 0.029, [illegible]
34,110	Al	0.042, 0.035
107	Ni-Al alloy	0.040
123	KH phthalate	0.040
63	$BaCl_2$	0.038
56	Li_2SO_4	0.037
70	NaBr	0.035
67	$CaCO_3$	0.034
79	CuCl	0.033
61	$MgSO_4$	0.029
105	Ag_2SO_4	0.025
102	$CaCO_3$	0.019
124	KIO_3	0.018
126	$KBrO_3$	0.018
103	Sb_2O_5	0.017
53	Cu	0.017
73	NaI	0.014

TABLE 5 (cont'd)

Run No.	Catalyst	k (hr^{-1})
89	$PbSO_4$	0.009
68	K_2CO_3	0.008
62	$Ba(NO_3)_2$	0.007
112	$K_2Cr_2O_7$	0.006
106	$Na_4P_2O_7$	0.006
43	KNO_3	0.004
44	K_2CrO_4	0.004
50	Zn	0.004
51	Mg	0.004
178,69	Na_2CO_3	0.004, 0.002
179	$NaHCO_3$	0.004
93	$ZnSO_4$	0.004
78	Pb_3O_4	0.002
86	LiOH	0.002
90	Li_2CO_3	0.002
91	Sb_2O_3	0.002

FIGURE 1

Typical Kinetic Curves
for
$KClO_4$ - pDVB - catalyst mixtures @ 350°C
$KClO_4$:pDVB = 5:1 (w/w)
catalyst:$KClO_4$ = 0.028:1 (w/w)

Run No.	Symbol	Catalyst
39	⊘	None
139	○	None
102	⊗	$CaCO_3$
112	⊕	$K_2Cr_2O_7$
81	◑	$Al_2(SO_4)_3$
71	◐	$Al_2(SO_4)_3$
97	◓	$Al_2(SO_4)_3$
54B	◬	KBr
34	⦶	Al
86	●	LiOH
38	⛛	V_2O_5
94	◒	$FeCl_2$
42	⊖	$Fe_2(SO_4)_3$

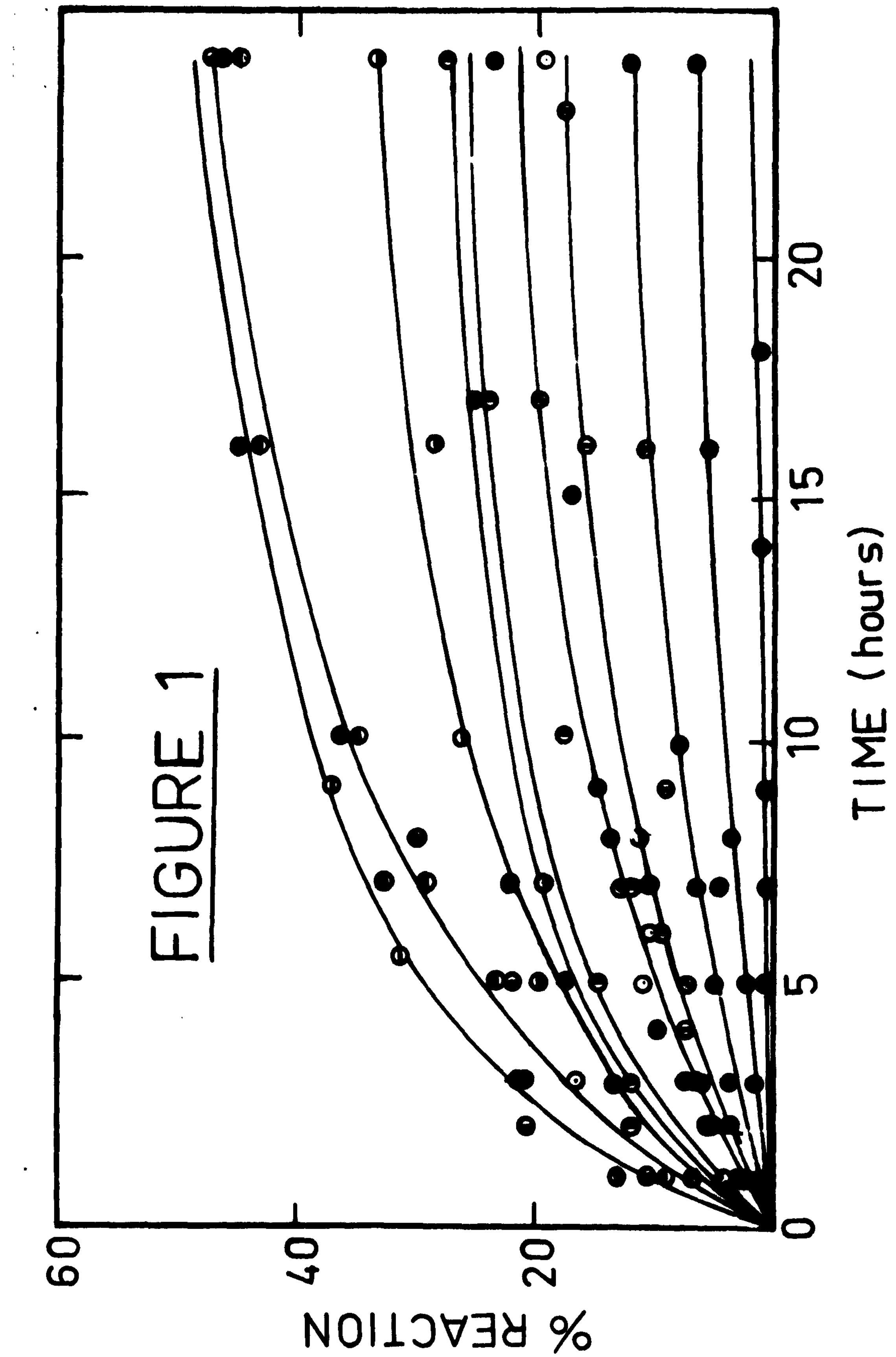


FIGURE 1

Since the solid products of the reaction are KCl and an oxidized polymer (plus water and carbon dioxide) the influence would be one of inhibition, mostly due to the KCl, acting as a barrier to further reaction.

If the catalysts are in small amounts the above considerations will hold true in the catalyzed reaction since the effect of the catalysts should be only to enhance the mobility of the oxidant and the inhibitory influence of the products should remain proportionally the same.

The general form of the rate equation should be of the type $dx/dt = k(a-x)^m/x^n$ where $m \leq 1$ and $n \leq 1$. The term x^n makes allowance for the inhibition of the diffusion of the product. By testing various equations of this type (see Tables 6, 7 pages 27, 28) it was found that the equation gave the best fit to the curves of both the catalyzed and the uncatalyzed reactions when $m = 1$ and $n = {}^2/3$.

The differential equation

$$dx/dt = \frac{k(a-x)}{x^{2/3}}$$

was used in the form

$$K = \frac{x^{5/3}}{a^3}\left(\frac{3}{5}a^2 + \frac{3}{8}ax + \frac{3}{11}x^2 + \ldots\ldots\right)/t$$

obtained by integrating the geometrical series expansion of the differential equation (see Experimental Part).

TABLE 6

	Empirical Equation $\quad kdt = x^n/(a-x)^m\,dx$
I	$kdt = \left[x^{1/3} / (a-x)^{2/3}\right] dx$ or $kt = x^{4/3}\,(3/4\,a^2 + 2/7\,ax + 1/6\,x^2 + \ldots) / a^{8/3}$
II	$kdt = \left[1 / (a-x)\right] dx$ or $kt = 2.303 \log\left[a/(a-x)\right]$
III	$kdt = \left[x^{1/5} / (a-x)\right] dx$ or $kt = x^{6/5}\,(5/6\,a^2 + 5/11\,ax + 5/16\,x^2 + \ldots) / a^3$
IV	$kdt = \left[x^{1/3} / (a-x)\right] dx$ or $kt = x^{4/3}\,(3/4\,a^2 + 3/7\,ax + 3/10\,x^2 + \ldots) / a^3$
V	$kdt = \left[x^{2/3} / (a-x)\right] dx$ or $kt = x^{5/3}\,(3/5\,a^2 + 3/8\,ax + 3/11\,x^2 + \ldots) / a^3$
VI	$kdt = \left[x^{3/4} / (a-x)\right] dx$ or $kt = x^{7/4}\,(4/7\,a^2 + 4/11\,ax + 4/15\,x^2 + \ldots) / a^3$
VII	$kdt = \left[x^{9/10} / (a-x)\right] dx$ or $kt = x^{19/10}\,(10/19\,a^2 + 10/29\,ax + 10/39\,x^2 + \ldots) / a^3$
VIII	$kdt = \left[x / (a-x)\right] dx$ or $kt = x \ln\left[a/(a-x)\right] - x$
IX	$kdt = \left[x^{4/3} / (a-x)\right] dx$ or $kt = x^{7/3}\,(3/7\,a^2 + 3/10\,ax + 3/13\,x^2 + \ldots) / a^3$

TABLE 7

Fit of Kinetic Data to Equations of Table 6 (for runs N.H.45)

Eqn's	X %	10	15	20	25	30	35	40	45	50	55	60
	t(hrs.)	0.50	0.80	1.10	1.50	2.05	2.75	3.50	4.50	5.60	6.90	8.40
I	kt	0.780	1.37	2.05	2.82	3.69	4.62	5.65	6.78	8.00	9.30	10.70
	k	1.56	1.71	1.86	1.95	1.79	1.68	1.61	1.51	1.43	1.35	1.28
II	kt	0.1060	0.1625	0.223	0.287	0.358	0.430	0.510	0.598	0.695	0.799	0.915
	k	0.213	0.203	0.202	0.192	0.175	0.156	0.146	0.133	0.124	0.116	0.109
III	kt	0.140	0.234	0.342	0.460	0.590	0.740	0.891	1.06	1.24	1.44	1.66
	k	0.280	0.292	0.311	0.306	0.288	0.269	0.255	0.236	0.222	0.209	0.198
IV	kt	0.171	0.301	0.456	0.634	0.835	1.10	1.325	1.60	1.91	2.27	2.62
	k	0.342	0.377	0.415	0.422	0.466	0.400	0.379	0.355	0.341	0.329	0.312
V	kt	0.297	0.598	1.005	1.49	2.13	2.84	3.70	4.63	5.65	7.06	8.40
	k	0.594	0.750	0.915	0.995	1.04	1.03	1.06	1.03	1.01	1.02	1.00

TABLE 7 (cont'd)

Equ'n	X %	10	15	20	25	30	35	40	45	50	55	60
	t(hrs.)	0.50	0.80	1.10	1.50	2.05	2.75	3.50	4.50	5.60	6.90	8.40
VI	kt	0.322	0.724	1.24	1.90	2.72	3.68	4.85	6.18	7.71	9.45	11.50
	k	0.644	0.905	1.13	1.26	1.33	1.34	1.39	1.37	1.37	1.37	1.37
VII	kt	0.446	1.000	1.795	2.840	4.25	5.82	7.80	10.15	12.90	16.10	19.70
	k	0.892	1.25	1.63	1.89	2.07	2.12	2.23	2.25	2.31	2.33	2.34
VIII	kt	0.60	1.25	2.30	3.87	5.80	8.0	11.0	14.8	19.5	24.0	31.5
	k	1.20	1.56	2.09	2.58	2.83	2.91	3.14	3.29	3.48	3.61	3.75
IX	kt	0.975	2.67	5.44	9.49	15.2	22.5	32.1	44.1	58.5	76.5	97.5
	k	1.950	3.34	4.94	6.32	7.40	8.19	9.17	9.80	10.4	11.1	11.6

The kinetic data for uncatalyzed reactions between pDVB and $KClO_4$ was fitted to equations V and VI. As for the catalyzed reactions, the empirical equation V gave a better fit for all the runs (Table 8, page 30).

(d) Effect of Catalyst Concentration

There appears to be a limiting catalyst concentration (Tables 9A, 9B, pages 31, 32 and Figure 2, page 34) above which the rate of reaction is not increased further. It is quite probable that at even higher catalyst concentrations the added substance would act as a barrier to the diffusing particles. We believe that at higher catalyst concentrations additional complicating effects may become operative, such as reaction between the 'catalyst' and $KClO_4$ and/or pDVB. Some of the catalysts are oxidizing agents (Fe^{+++} salts, V_2O_5, etc.), others are reducing agents (metals) and accordingly in the presence of large concentrations of these substances the whole picture of the reaction may change.

(e) Blank Determinations

Experiments carried out on $KClO_4$-catalyst mixtures (without pDVB) under the usual experimental conditions (Table 10, page 36) showed that certain catalysts caused a decomposition of $KClO_4$ These catalysts were used at lower temperatures

TABLE 8

Comparison of Fit of Uncatalyzed Reactions* to Equations V, VI

		Run No. 31		Run No. 40		Run No. X		Run No. 39	
X	$k_V t$	t(hrs)	k(hr^{-1})	t	k	t	k	t	k
10	0.297	5.0	0.059	5.40	0.055	4.0	0.074	5.3	0.056
15	0.598	10.0	0.060	10.50	0.057	7.50	0.080	9.25	0.065
20	1.005	16.0	0.063			12.25	0.082	16.7	0.060
25	1.49	24.0	0.062			20.30	0.073		
30	2.13	32.0	0.067						
35	2.84	44.0	0.065						
40	3.70								
		ave =	0.063	ave =	0.056	ave =	0.077	ave =	0.060

		Run No. 31		Run No. 40		Run No. X		Run No. 39	
X	$k_{VI} t$	t(hrs)	k(hr^{-1})	t	k	t	k	t	k
10	0.322	5.0	0.064	5.40	0.060	4.0	0.080	5.3	0.061
15	0.724	10.0	0.072	10.50	0.069	7.50	0.096	9.25	0.078
20	1.24	16.0	0.077			12.25	0.101	16.7	0.074
25	1.90	24.0	0.079			20.30	0.093		
30	2.72	32.0	0.085						
35	3.68	44.0	0.084						
40	4.85								
		ave =	0.077	ave =	0.064	ave =	0.092	ave =	0.074

---

* The ratios of $KClO_4$ to pDVB for Runs 31, 39, 40 and X are 2.5:1, 5:1, 5:1, and 1:1, respectively

TABLE 9 A

Effect of Catalyst Concentration on Rate of Reaction

$KClO_4$:pDVB $\cong$ 5:1 (w/w) @ 350°C

Run No.	$\% V_2O_5$ in Mixture	k (hr^{-1})
139	0	0.041
133	0.1	0.084
134	0.2	0.112
135	0.4	0.120
136	1.0	0.120
137	2.0	0.120
138	4.0	0.120

TABLE 9 B

Effect of Catalyst Concentration
on the Reaction between $KClO_4$ and pDVB

Run No.	Catalyst	$KClO_4$:pDVB	Catalyst :pDVB	Temp.	k (hr^{-1})
E	V_2O_5	2.5:1	0.14:1	350°	0.87
F	"	"	0.028:1	"	0.58
31	None	"	0	"	0.063
L	Al powder	5:1	0.028:1	400°	0.74
P	"	"	0.007:1	"	0.56
K	None	"	0	"	0.46
59	Fe powder	5:1	0.112:1	350°	0.065
52	"	"	0.028:1	"	0.070
60	"	"	0.007:1	"	0.081
39	None	"	0	"	0.060

FIGURE 2

The Effect of Catalyst Concentration
on the Reaction
between
$KClO_4$ and pDVB

k (hr^{-1}) vs % Catalyst (V_2O_5)

$KClO_4$:pDVB = 5:1 (w/w)
Temp. = 350°C

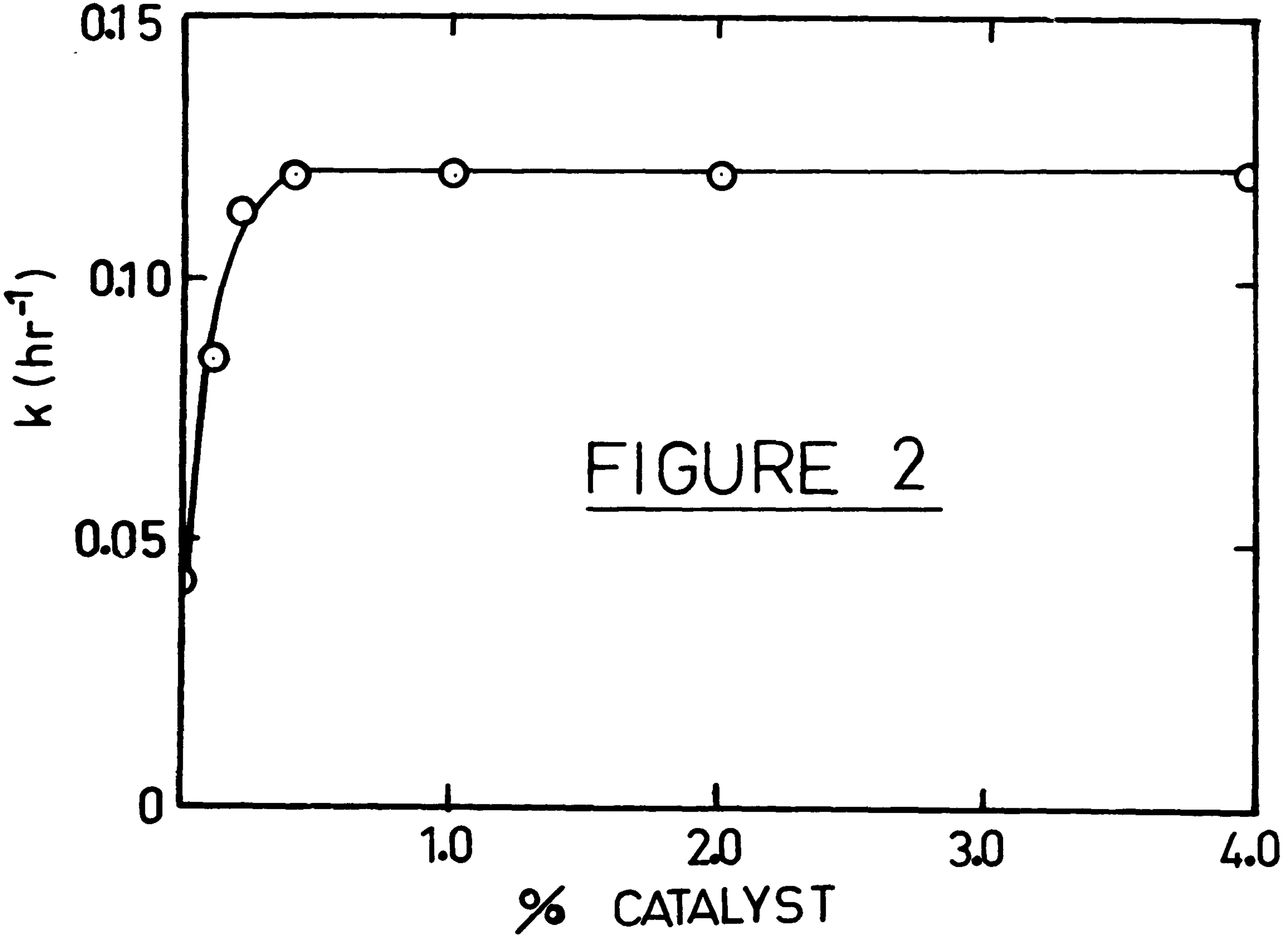


FIGURE 2

for the oxidation reactions with pDVB but the possibility cannot be ruled out that the alteration of conditions in the course of the reaction might enable these catalysts to resume their effect. The table shows that only LiCl had a significant decomposition effect in closed tubes and this occurred at 400°C. Vanadium pentoxide at 400°, but in a reaction chamber open to the atmosphere had a large decomposition effect. In closed tubes at 400° the decomposition of $KClO_4$ with V_2O_5 was insignificant over 24 hours. All other substances tested under the same conditions showed little or no decomposition of $KClO_4$.

Runs made to determine the decomposition of the polymer showed that it commenced only at 400°C over extended periods of heating in the presence of air. The weight loss of the polymer indicated a thermal decomposition of up to 30% over 24 hours at this temperature. As nearly all runs with oxidants were performed at a much lower temperature and in sealed ampoules the thermal decomposition of the polymer can be neglected.

The amount of reaction of $KClO_4$ with KCl formed, at the temperatures used, is negligible. The eutectic temperatures given in the literature (Schroder(53)) for mixtures of $KClO_4$ and KCl are much higher than the reaction temperatures used.

TABLE 10

Blank Determinations

$KClO_4$ - added substance (without substrate)

Run No.	Added Substance	Conc. of Added Substance	Reaction Temp. (°C)	Reaction Time (hrs)	% Decomp. of $KClO_4$
161	NH_4Cl	2% (by wt.)	250	24	0
	"	"	300	"	0
	"	"	400	"	5.7
175	H_3PO_4	0.005 ml/ 0.15-0.25g $KClO_4$	400,350,300	5	0
			400,350,300	16	0
N-A	$Fe_2(SO_4)_3$	2%	400	24	0, 2.2
			350	23	0, 0
26	Al	2%	400	72	4.7, 2.1
	"	"	"	24	0.4, 1.2
27 A	LiCl	2%	400	10	35.6
	"	"	"	24	43.5,40.3
27 B	V_2O_5	2%	400	24	2.2, 1.6
25	V_2O_5	2%	400	66	12.3
24	open tubes V_2O_5	2%	400	16	18.5
22 A	V_2O_5	"	"	"	15.3
23	V_2O_5	2%	400	16	1 - 4
		"	"	"	1.35, [illegible]
22 B	K_2CO_3	2%	400	16	0.1
			350	44	1.3
23 - 6	$FeCl_2$	2%	350	8	0

(f) Reproducibility and Experimental Error

Reproducibility of results for reactions between $KClO_4$ and pDVB together with added substances depends on the following physical factors:

(1) Uniformity of grain size (i.e. surface area).

(2) Uniformity of mixing and pressing of pellets.

(3) Temperature control.

(4) Aging of tablets.

It is to be expected that strict control of all these conditions is practically impossible and that in solid-solid reactions reproducibility of results will be relatively poor. Table 5, page 22 includes duplicates of some experiments and shows that the variation between the values of k may in some cases be considerable. Figure 1, page 16, shows that in any one run the points gave a fairly smooth curve with only one or two points wildly off the curve. Thus, for a set of conditions as set for a particular run the reproducibility is good. In most cases, especially if the reaction was fast, two or more runs were made under duplicated conditions and the reaction curves were drawn so as to give the best fit to all experimental points.

IIB The Catalysis of the pDVB-$KClO_3$ Reaction

[illegible] Ignition Temperatures

An examination of the ignition times at corresponding temperatures (Table 11, page 39) reveals that the mixtures containing a strong catalyst ignited much more quickly than those containing a weak catalyst or inhibitor. The only exception to this rule was LiCl which, although it acted as a medium strong catalyst, (see part II-B-(b)) was in the ignition test not conducive to a rapid ignition.

Most of the ignitions were preceded by a gentle burning which in a few seconds developed into a rapid burning accompanied by smoke and flame. There was an exception in the samples containing $CoSO_4$ which did not ignite in this manner but with a sudden explosion. Moreover, it had one of the lowest of ignition temperatures, slightly lower than for mixtures containing stronger catalysts such as $MnSO_4$, $MnCl_2$ and NH_4Cl.

Some mixtures containing inhibitors did not ignite but fused and probably decomposed in the melt.

(b) The effects of various added substances on the $KClO_3$-pDVB reaction are shown in Tables 12, 13, pages 42 & 43 and Figure 3, page45. As in the catalyzed $KClO_4$-pDVB reaction there are

TABLE 11

Ignition Times (seconds) ($KClO_3$ + pDVB + catalysts)

Sample No.	Catalyst	Temp. °C →	260	270	275	280	290	300	310	315	320	325	330	340
29	$CoSO_4$					50	47	35	26		27	40	16	
13	$MnCl_2$						63	40	38		26		20	
38	$MnCl_2$					75	59	48	48		39		22	
55	$CoSO_4$		84	50			34		25				23	
9	NH_4Cl					55	55	39	30		33		25	
39	NH_4Cl					47	45 40	40	33		25		29	23
40,19	NH_4Br			90				50 59	51 53		44		26 33	
50	$CuCl_2$			95			54		34				27	
33	$CuCl_2$			97		72	63	52	37			36	33	
44	$Al_2(SO_4)_3$			120 120				64	67				28	
4	$Al_2(SO_4)_3$				108		81		55				39	
29	$Al_2(SO_4)_3$							85 71	55		55		42 43	
45	$Fe_2(SO_4)_3$			97			60		45				29	
3	$Fe_2(SO_4)_3$			90			50		47				31	
30	$Fe_2(SO_4)_3$					104	58	48	45		31		37	

TABLE 11 (cont'd)

Sample No.	Catalyst	Temp. °C →	260	270	275	280	290	300	310	315	320	325	330	340
2	V_2O_5			144			60		48				30	
46	V_2O_5				162		68		45				34	
27	V_2O_5							58 53	36 40		35 30		30	
43	$K_2Cr_2O_7$			92			68		54				33	
19	$K_2Cr_2O_7$						61	42	32		35 42 42		42	
47	$MnSO_4$			132			65		49				35	
42	$MnSO_4$			114				50	45		48			
21	$MnSO_4$					72	57	52	47		32		32	
31	CuCl						95	67	56		55		37	
12	CuCl					89	100	48 48	51		44		39	
48	$NiSO_4$			$240^{Ü}$					57 66				47	
34	$NiSO_4$					100	91	55	59		54		52	
8,36	LiCl											138 180^{M}		
20	$ZnSO_4$									240^{M}				[illegible]
14	NaCl												140	
15	KI												155	

TABLE 11 (cont'd)

Sample No.	Catalyst	Temp. °C →	260	270	275	280	290	300	310	315	320	325	330	340
22	$PbSO_4$												240^M	
26	$CaSO_4$													180^M
32	$PbCl_2$												180^M	
25	Na_2SO_4												240^M	
23	KNO_3												240^M	
37	Li_2SO_4												240^M	
35	$BaCl_2$												240^M	
10	LiOH												240^U	
11	Cu												240^U	
41	$MgSO_4 \cdot 7H_2O$										240^M			
16	Al												240^U	
24	Na_2CO_3												180^U	
17	Zn												180^U	
	No catalyst												113	

M - melted

U - unmelted

specific effects. Strongly acidic substances strongly catalyze and strongly basic substances strongly inhibit. There is a finer gradation between these experiments as compared with the $KClO_4$ reactions as the gap between the amount of reaction for a highly activated reaction and an uncatalyzed reaction is much larger. Here we see that some metals catalyze the reaction (e.g. aluminum) to an appreciable extent and others not at all.

The highest degree of catalysis was obtained with ammonium bromide, the rate of reaction at 225° being 230 times that of the uncatalyzed reaction at 250°. A similar rate was obtained for ammonium chloride and about 1/3 of this rate for aluminum sulfate, manganese sulfate, ferric sulfate and cobalt sulfate. At 225° vanadium pentoxide catalyzed the rate to five times the uncatalyzed rate at 250°. At 225° the uncatalyzed reaction between $KClO_3$ and pDVB did not proceed.

In general, salts of the heavy metals were strong catalysts for the $KClO_3$-pDVB reactions much as they were for the $KClO_4$-pDVB reaction and salts of the alkali metals were either weak catalysts or inactive. It can be stated that the qualitative effect of catalysts and inhibitors was the same with $KClO_4$ and $KClO_3$, but the quantitative relations differed widely.

Experiments were run under identical conditions for examination of the products from the standpoint of oxygen incorporated

TABLE 12

Effect of Catalysts

@ 225°C

$KClO_3$:pDVB = 5:1 (w/w)

Catalyst:$KClO_3$ = 0.028:1 (w/w)

Run No.	Catalyst	ka (hr^{-1})
19,40	NH_4Br	15.4, 5.6
39	NH_4Cl	13.3
42,47	$MnSO_4$	4.5, 4.5
45A,45B	$Fe_2(SO_4)_3$	3.03, 3.03
29	$CoSO_4$	2.06
44A,44B	$Al_2(SO_4)_3$	1.92, 1.92
51,52	V_2O_5	0.33, 0.33 (Initial Rate)
	None	0.00

TABLE 13

Effect of Catalysts

@ 250°C

$KClO_3$:pDVB = 5:1 (w/w)

Catalyst:$KClO_3$ = 0.028:1 (w/w)

Run No.	Catalyst	ka (hr^{-1})
13	$MnCl_2$	85.0
21	$MnSO_4$	28.6
5	$CoSO_4$	20.0
4,28	$Al_2(SO_4)_3$	11.1, 10.0
27,53,54,46	V_2O_5	10 (initial rate)
30,3	$Fe_2(SO_4)_3$	10, 9.1
50,33	$CuCl_2$	5.0, 3.70

TABLE 13 (cont'd)

Run No.	Catalyst	k_o (hr^{-1})
8, 36	LiCl	3.2, 1.92
34,48,6	$NiSO_4$	2.42, 2.42, 1.0
41	$MgSO_4 \cdot 7H_2O$	1.44
12,31	CuCl	1.25, 1.2
18,43	$K_2Cr_2O_7$	0.98
37,49	Li_2SO_4	0.642
20	$ZnSO_4$	0.54
16	Al	0.30
7	Fe	0.20
25	Na_2SO_4	0.134
15	KI	0.134
1	None	0.066
128,129	MnO_2	0.066
35	$BaCl_2$	0.066
32	$PbCl_2$	0.066
11	Cu	0.066
26	$CaSO_4$	0.066
22	$PbSO_4$	0.066
14	NaCl	0.066
17	Zn	0.02
23	KNO_3	0.02
10	LiOH	0.00
24	Na_2CO_3	0.00

FIGURE 3

Typical Kinetic Curves

for

$KClO_3$ - pDVB - catalyst mixtures @ 225°C

$KClO_3$:pDVB = 5:1 (w/w)

catalyst:$KClO_3$ = 0.028:1 (w/w)

Run No.	Symbol	Catalyst
45 A	●	$Fe_2(SO_4)_3$
45 B	○	"
29	⊕	$CuSO_4$
44 A	◑	$Al_2(SO_4)_3$
44 B	⊗	"
38	◓	$MnCl_2$

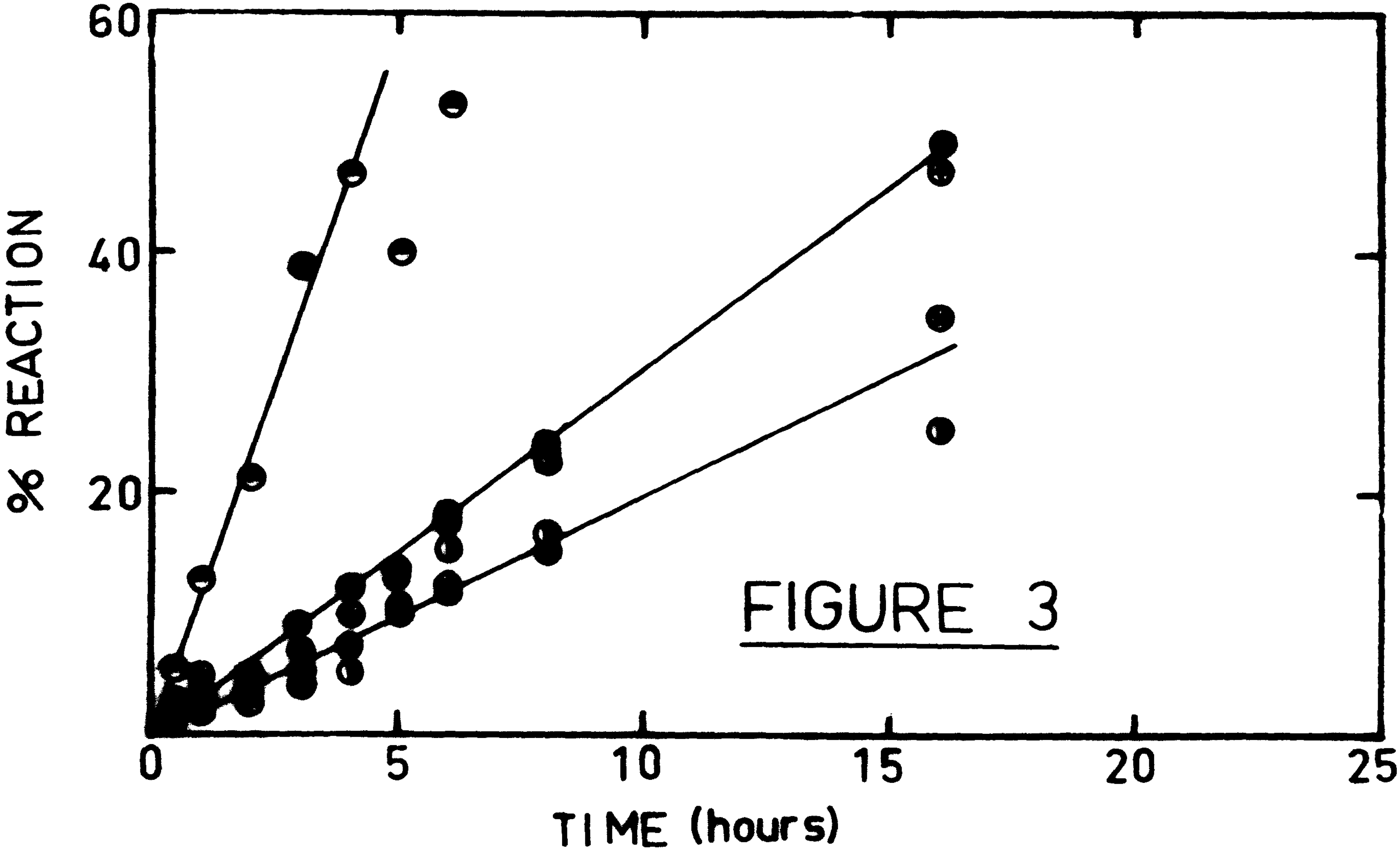


FIGURE 3

into the polymer. The amount of change in the elementary composition (see Table 14, page 47) is proportional to the amount of $KClO_3$ decomposed. It is not equal to the latter since the reaction is not solely an incorporation of oxygen into the polymer molecule, but is accompanied by the formation of carbon dioxide and water.

Glasner and Weidenfeld(18) found that in the thermal decomposition of $KClO_3$ and $KClO_3$-KCl mixtures two consecutive reactions took place:

$$KClO_3 \rightarrow KCl + 3O$$

$$\text{and } KCl + 4O \rightarrow KClO_4$$

These reactions took place at temperatures higher than 455°C. The formation of $KClO_4$ in the thermal decomposition of $KClO_3$ is confirmed by A. E. Harvey et al(21), again occurring only at temperatures in the neighborhood of 500°C. Vanden Bosch and Aten(61) found contrary data with labeled oxygen in chlorate which did not appear in perchlorate.

The present reactions between $KClO_3$ and pDVB in the presence of catalysts took place at 250° and lower and proceeded to a complete decomposition to KCl. It is unlikely that $KClO_4$ could be formed for the reason that it would not react at the above temperature. Thus the second of the above reactions does not take place here. The oxygen formed by the first reaction probably moves to the substrate as O_2^- or O^- where part of it is incorporated into the polymer molecule and part forms CO_2 and H_2O with the substrate.

TABLE 14

Comparison of Oxygen Incorporated into pDVB with Oxygen Evolved from $KClO_3$

Sample No.	% Reaction (Cl^- analysis)	pDVB product Analysis C	H	O (by difference)	A	B	A/B
334	0	89.34	8.53	2.13			
337	24.3	84.79	7.51	7.70 (5.57)	0.475	0.0590	8.1
336	54.4	78.01	6.37	15.62 (13.49)	1.07	0.156	6.9

A = g O liberated (from Cl^- analysis)

B = g O incorporated into pDVB

The reaction of $KClO_3$ with pDVB in the presence of vanadium pentoxide showed the existence of an initiation period for the reaction. At 250°C the reaction proceeds to about 15% after 3.5–5 hours and between the fourth and fifth hour of heating another 60% of reaction takes place. The rate then levels off again.

At 225°C the initiation period for this reaction lasts more than 20 hours after which the reaction rate again climbs rapidly.

This was the only case investigated wherein sigmoid reaction curves with initiation periods were found. Curves of this type are common in thermal decompositions but we are unable to propose any explanation for its occurrence here in the presence of V_2O_5 while all other added substances showed no initiation period. Also, no such effect of V_2O_5 was found in the $KClO_4$-pDVB reaction.

(c) Effect of Catalyst Concentration

Table 15, page 49 and Figure 4, page 51 show that the increase in the reaction rate is on the average three-fold for a doubling of the catalyst concentration and does not reach a maximum effect for the catalyst concentration used (up to 2% of the pDVB-$KClO_3$ mixture by weight).

TABLE 15

Effect of Catalyst Concentration

$KClO_3$:pDVB = 5:1
Temp. 250°C

Run No.	Catalyst:($KClO_3$+pDVB) ($MnSO_4$)	kp (hr^{-1})
150	0	0.10
151	0.05	0.37
152	0.2	1.34
154	0.4	3.03
156	0.8	10.5
153	1.0	11.8
155	2.0	40.0

FIGURE 4

The Effect of Catalyst Concentration
on the Reaction
between
$KClO_3$ and pDVB

K_o (hr^{-1}) vs % Catalyst ($MnSO_4$)

$KClO_3$:pDVB = 5:1 (w/w)

Temp. = 250°C

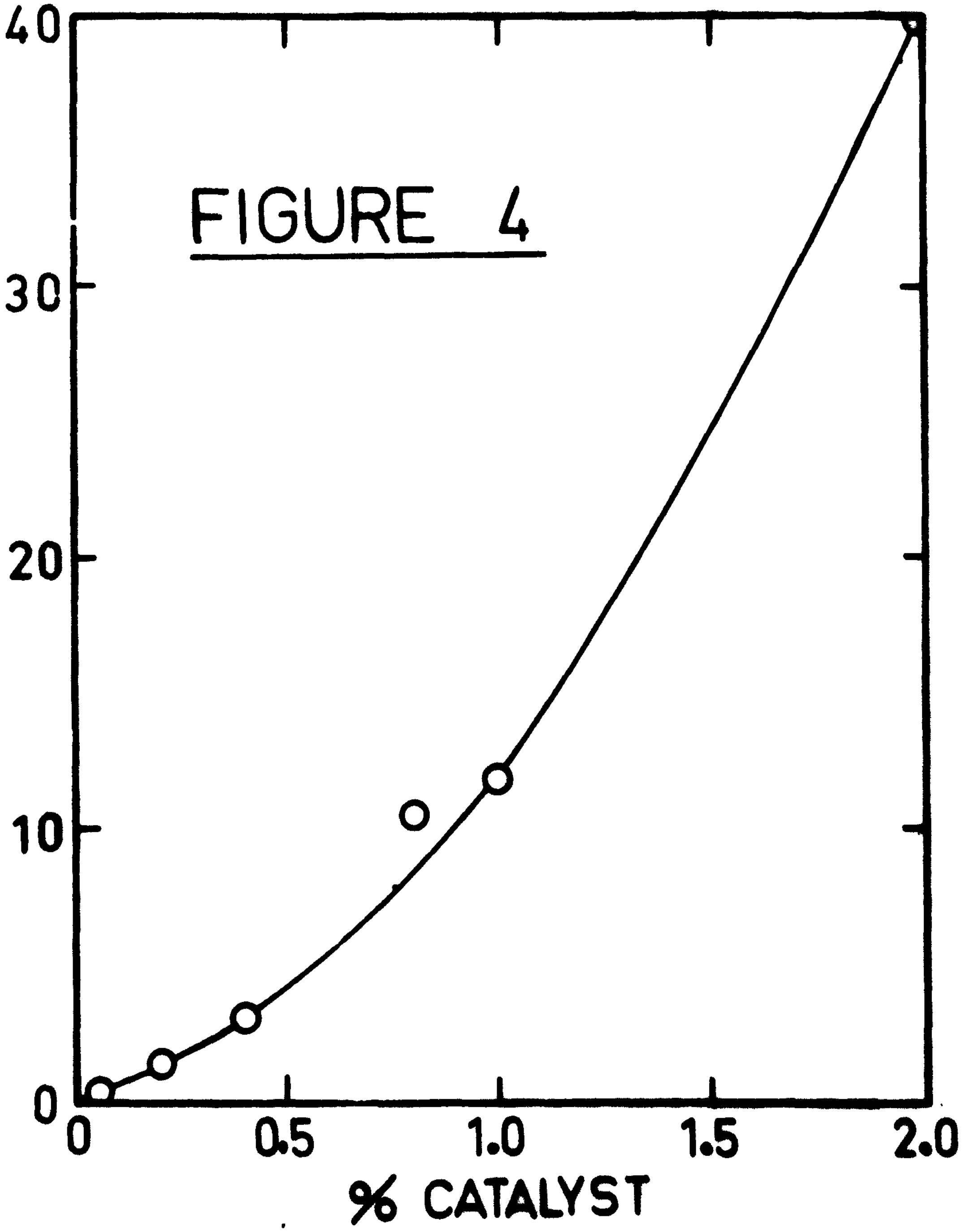


FIGURE 4

(d) Kinetics and Rate Law

The reaction of $KClO_3$ with pDVB was found to be of zero order in $KClO_3$, i.e.,

$$\frac{dx}{dt} = k$$

$KClO_3$ is the only oxidant with which this relationship is valid. $KClO_4$, $KBrO_3$ and KIO_3 (see below) all give rates corresponding to Eq. V. This would mean that in the case of $KClO_3$ the transport of oxygen is very rapid and the reaction rate depends only on the availability of the substrate. In other words, the amount of $KClO_3$ (5 times the weight of the substrate) is in swamping excess in this case, eliminating the $KClO_3$ concentration from the equation.

(e) Blank Determinations

Table 16, page 53, shows that the decomposition of $KClO_3$-NH_4Cl mixtures at 225° was about 7% over 24 hours. This was also the temperature for the NH_4Cl-catalyzed reaction between $KClO_3$ and pDVB. The amount of side-reaction is thus not negligible even if it is very much smaller than the reaction rate. All other substances showed only slight interaction with $KClO_3$ at 250°, the maximum temperature used for the $KClO_3$-pDVB reactions. It can therefore be stated that there were no side reactions between $KClO_3$ and the added inorganic substances.

TABLE 16

Blank Determinations

$KClO_3$ - added substance (without substrate)

Run No.	Added Substance	Conc. of Added Substance	Reaction Temp. (°C)	Reaction Time (hrs)	% Decomp. of $KClO_3$
160	NH_4Cl	2%	250	24	36.7
	NH_4Cl	2%	300	24	97
	NH_4Cl	2%	230	24	5.9, 7.6
162	$MnSO_4$	2%	250	24	1.1
	$MnSO_4$	2%	300	24	42.5,42.3
	$MnSO_4$	2%	230	24	0,0
167	None	2%	250	24	0
		2%	300	24	0.8, 0.9
open tubes	V_2O_5	2%	250	18	0
	V_2O_5	2%	250	21	0

(f) Reproducibility and Experimental Error

The reproducibility of the kinetic runs using $KClO_3$ as the oxidant was in general better than with $KClO_4$ as oxidant. The factors accounting for this are the greater stability of the $KClO_3$-compounded pellets and the more accurate control of temperature of reaction at lower temperatures as were used in the $KClO_3$ reactions. Table 12, page 42, shows that for two runs using NH_4Br as the added substance, the reproducibility was bad but Tables 12 and 13 show that all other duplicated runs were almost identical. Within any particular kinetic run the separate points fell on or very close to a straight line (Figure 3, page45).

II C Potassium Iodate as Oxidant

(a) Effects of Catalysts

Table 17, page 57, and Figure 5, page 59, show the nature and extent of the effects of added substances to the reaction between KIO_3 and pDVB. A smaller number of catalysts were tried, being mostly those which catalyzed the previous reactions strongly.

Reactions were carried out under the same operating conditions as before but samples were made up in a ratio of 10 parts KIO_3 to 1 part pDVB by weight, for greater mechanical stability of the pellets and a closer parallel of the molar ratios. The catalyst to oxidant ratio remained 0.028 parts to one part oxidant by weight. The temperature chosen for the reaction was lower than for the $KClO_4$ reaction and higher than for the $KClO_3$ reaction, a consideration due to the relative speed of each reaction.

The reaction was catalyzed up to 100 times the uncatalyzed rate by $MnSO_4$ and to lesser degrees by $CoSO_4$, $Al_2(SO_4)_3$ and NH_4Br, in descending order.

As in the case of $KClO_3$, there exists a qualitative agreement in the effects of the various additives with their effects in the $KClO_4$ reaction.

(b) The kinetics and empirical rate law of the catalyzed KIO_3-pDVB reaction

The kinetic data gave a good fit to the empirical equation found for the $KClO_4$ oxidation of pDVB (Equation V). Therefore the same arguments hold for this reaction with regard to diffusion, mode of catalysis and interpretation of results.

TABLE 17

Effects of Catalysts

KIO_3:pDVB = 10:1 (w/w)

Catalyst:KIO_3 = 0.028:1 (w/w)

Temp. - 325°C

Run No.	Catalyst	k (hr^{-1})
16	$MnSO_4$	0.743
15	$CoSO_4$	0.236
17	$Al_2(SO_4)_3$	0.112
22	$Fe_2(SO_4)_3$	0.109
20,21	NH_4Br	0.085, 0.085
11,18,19	None	0.01 *

*average of three experiments, giving individual rates 0.016, 0.007, 0.007

FIGURE 5

Typical Kinetic Curves
for
KIO_3 - pDVB - catalyst mixtures @ 325°C
KIO_3:pDVB = 10:1 (w/w)
catalyst:KIO_3 = 0.028:1 (w/w)

Run No.	Symbol	Catalyst
18	●	None
19	○	None
20	⊗	NH_4Br
21	⊕	NH_4Br
22	⦶	$Fe_2(SO_4)_3$
16	◑	$MnSO_4$
15	⊖	$CoSO_4$

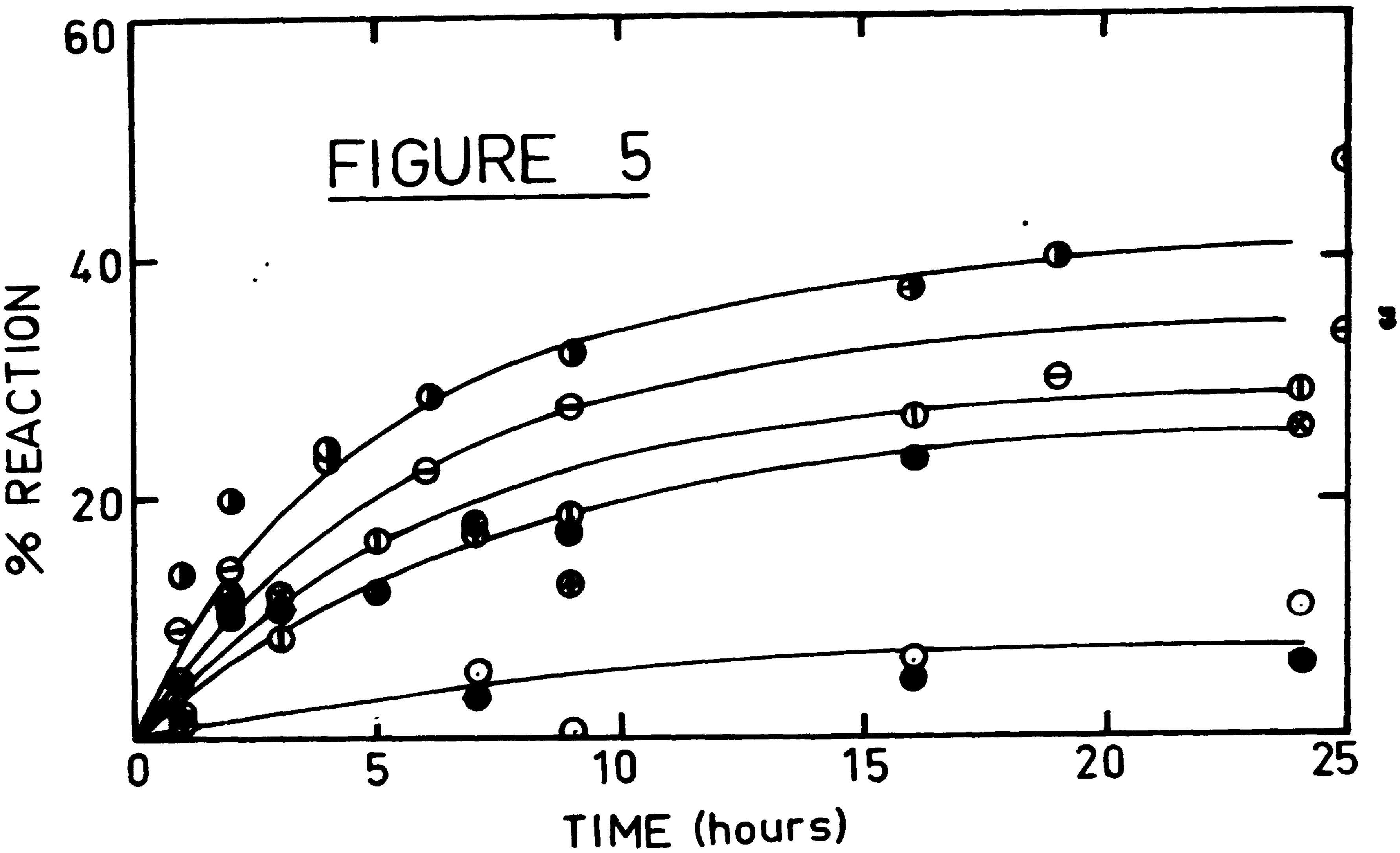


FIGURE 5

II D $KBrO_3$ as oxidant

(a) Ignition times

Table 18 page 61, shows a close agreement between the ignition times and the kinetic results for the same mixtures. The strong catalysts promoted rapid ignition and the inhibitors prevented ignition. The table shows that the reaction temperature used in the kinetic runs was below the ignition temperatures but for the strong catalysts the reaction temperatures and the ignition temperatures were very close. As the kinetic runs were performed in vacuum and the ignition temperatures were found for samples open to the atmosphere the influence of atmospheric oxygen is evident.

(b) Effect of Catalysts; Kinetics and Rate Law.

The empirical rate law of the catalyzed $KBrO_3$-pDVB reaction was the same as for the $KClO_4$ and KIO_3 oxidations.

Reactions were carried out under the same conditions, the temperature of reaction being the only change. This was lower than for the $KClO_4$ and KIO_3 oxidations because of the greater ease of $KBrO_3$ oxidation. Runs were made at 300° and at 275°, the lower temperatures for those catalysts which drove the reaction too quickly for a proper evaluation and the higher temperature for the less active catalysts.

TABLE 18

Ignition Times (Seconds) ($KBrO_3$ + pDVB + catalysts)

Sample No.	Catalyst	Temp. °C →	260	270	280	290	295	300	305	310	315	320	325	330	335	340	350	360
25	$MnCl_2$											20		16				
16	$CoSO_4$		240*	94	52	47		31	29			23	22				13	
28	[illegible]					44			28		24	24		25				
[illegible]	$Al_2(SO_4)_3$							55	43			26		30				13
24	[illegible]				240*		44	29		28		27			28			
[illegible]	[illegible]					240*				37		28				18	13	
[illegible]	[illegible]														19		13	
	[illegible]									54		54		30			28	
[illegible]	[illegible]											74		58			56	
[illegible]	[illegible]											113		68			52	
22	[illegible]											240*						
[illegible]	[illegible]											240*						
[illegible]	[illegible]													240*				

* 240 seconds - samples did not ignite in this time

Table 19, page 63, and Figure 6, page 65, show that the catalysts which strongly or weakly catalyzed the $KClO_4$, $KClO_3$, KIO_3 reactions had a similar effect on the $KBrO_3$ oxidations. More specifically, $MnSO_4$, $Al_2(SO_4)_3$, $CoSO_4$, $MnCl_2$, $Fe_2(SO_4)_3$, NH_4Cl were powerful catalysts while alkali metal salts or bases or powdered metals were either weak catalysts or inhibitors.

TABLE 19

Effect of Catalysts

$KBrO_3$:pDVB = 5:1

Catalyst:$KBrO_3$ = 0.028:1

Temp. - 300°C

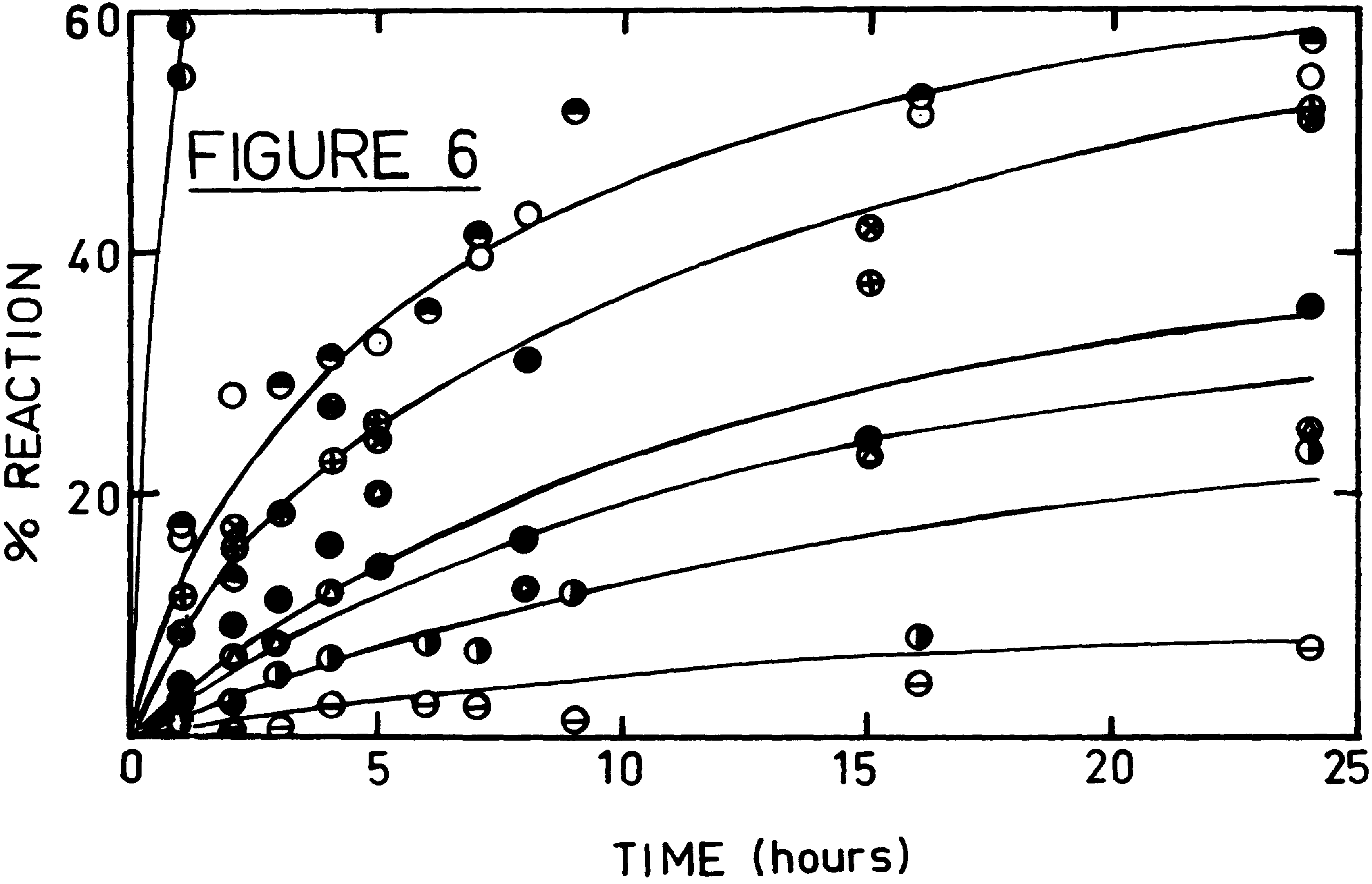
Run No.	Catalyst	k (hr^{-1})
18	NH_4Cl	7.98
16	$CoSO_4$	7.40
24	$NiSO_4 \cdot 6H_2O$	6.8
20,21	$Al_2(SO_4)_3$	0.526, 0.526
11,12	V_2O_5	0.273, 0.273
29	Li_2SO_4	0.23
10	None	0.116
17	KBr	0.115
15	KI	0.082
22	Cu	0.048
23	Na_2CO_3	0.006
	@ 275°C	
25,26	$MnCl_2$	5.20, 5.20
27,28	$MnSO_4$	5.20, 5.20
13,14	$Fe_2(SO_4)_3$	1.364, 1.364
19	$Al_2(SO_4)_3$	0.100

FIGURE 6

Typical Kinetic Curves
for
$KBrO_3$ - pDVB - catalyst mixtures @ 300°C
$KBrO_3$:pDVB = 5:1 (w/w)
catalyst:$KBrO_3$ = 0.028:1 (w/w)

Run No.	Symbol	Catalyst
10	●	None
11	⊗	V_2O_5
12	⊕	V_2O_5
15	◬	KI
20	◓	$Al_2(SO_4)_3$
21	○	$Al_2(SO_4)_3$
22	◑	Cu
23	⊖	Na_2CO_3
24	◐	$NiSO_4$

FIGURE 6



II E Comparison of Effects of Catalysts on Oxidation of pDVB by $KClO_4$, $KClO_3$, $KBrO_3$ and KIO_3

The relative rates of reactions with different oxidants and the same catalyst (Tables 20, 21, pages 68, 69) show that the influence of the catalyst, with a few exceptions, lies in the same direction. There is no quantitative agreement, however, between the different rates.

Several substances which did not greatly influence the rate of oxidation of pDVB by $KClO_4$ had a strong catalytic effect on the reaction with $KClO_3$, KIO_3 and $KBrO_3$. These were $CoSO_4$, $MnCl_2$, $MnSO_4$, NH_4Cl and NH_4Br.

Substances which strongly inhibited one reaction had the same effect on the other reactions and substances which catalyzed the $KClO_4$-pDVB reaction also catalyzed the other reactions.

The relative times of ignition using $KClO_4$, $KClO_3$ and $KBrO_3$ as oxidants with various catalysts (Table 22, page 70) show a closer agreement for the different oxidants and the same catalyst. Obviously, the solid-solid reaction rates and the ignition tests cannot be compared since in the latter case the reaction is strongly influenced by the presence of air. The substances used are in many cases catalysts for the air-oxidation reaction. (For example, in the oxidation of various forms of carbon by air it was found by Patai et al(45, 46) that bases were highly active catalysts by enhancing the breakdown of surface oxides which were formed on the substrates used).

Activation Energy

The values of the activation energy obtained for the catalyzed $KClO_4$-pDVB, $KClO_3$-pDVB and $KBrO_3$-pDVB reactions were respectively 43.0, 38.6 and 45.9 Kcal/mole with the catalysts $Fe_2(SO_4)_3$, $CoSO_4$ and $Al_2(SO_4)_3$ the respective catalysts. These were calculated from the values given in Table 23.

The respective values obtained for the uncatalyzed reactions* were 40.5, 45.4 and 43.1 K.cal. These values were obtained for ratios of $KClO_4$ to pDVB of 2.5:1 and of $KClO_3$ and $KBrO_3$ to pDVB of 6:1.

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* M. Albeck, private communication.

TABLE 20

Relative Rates

Added Substance	Oxidant and Reaction Temperature					
	$KClO_4$	$KClO_3$		$KBrO_3$		KIO_3
	350°	250°	225°'	300°	275°"	225°
None	1	1	—	1	—	1
$Fe_2(SO_4)_3$	5.8	150	46	—	11.3	10
$Al_2(SO_4)_3$	4.3	150	29	4.5	1	11
V_2O_5	3.0	150	5	2.4	—	—
$MnSO_4$	1.6	430	68	—	4.5	74
NH_4Cl	1.5	—	200	69	—	—
$NiSO_4$	1.3	37	—	59	—	—
NH_4Br	1.3	—	230	—	—	8.5
KBr	1	—	—	1	—	—
KCl	1	—	—	—	—	—
$CoSO_4$	0.9	300	43	64	—	24

' Relative to non-catalysed rate at 250°

" Relative to non-catalysed rate at 300°

TABLE 21

Relative Rates

Oxidant and Reaction Temperature

Added Substance	$KClO_4$ 350°	$KClO_3$ 250°	 225°	$KBrO_3$ 300°	 275°
None	1	1	—	1	—
Fe	1.2	3	—	—	—
$MnCl_2$	1.0	1300	190'	—	4.5"
Al	0.7	4.6	—	—	—
Li_2SO_4	0.6	11	—	2.0	—
$MgSO_4$	0.5	—	—	—	—
Na_2CO_3	0.05	0	—	0.005	—
LiOH	0.03	0	—	—	—
Cu	—	1	—	0.04	—

' Relative to non-catalysed rate at 300°

" Relative to non-catalysed rate at 250°

TABLE 22

Comparison of Ignition Times of Oxidant - pDVB - Catalyst Mixtures

(Ratio of Ignition Time for Mixture to Time for Uncatalyzed Mixture)

Catalyst	$KBrO_3$ 320°	$KClO_3$ 330°	$KClO_4$ 460°
$MnCl_2$	0.18	0.18	0.40
$CoSO_4$	0.20	0.20	0.32
$MnSO_4$	0.21	0.31	0.32
$Al_2(SO_4)_3$	0.25	0.36	0.18
$NiSO_4$	0.25	0.44	0.42
V_2O_5	0.25	0.28	—
$Fe_2(SO_4)_3$	0.25	0.27	—
Li_2SO_4	0.48	>2	1
KBr	0.65	—	1
None	1 (113 secs.)	1 (113 secs.)	1 (115 secs.)
Cu	2	>2	>2
KI	2	—	0.33
Na_2CO_3	[illegible]	>2	0.77

TABLE 23

Arrhenius Plots for Activation Energy of Catalysed Oxidant – pDVB Reactions

A. $KClO_4$ + pDVB + $Fe_2(SO_4)_3$

Temp. (°C)	1/T – abs.	k (hr^{-1})	ln k
250	1.91×10^{-3}	0.003	-5.81
300	1.745×10^{-3}	0.142	-1.95
350	1.605×10^{-3}	1.0	0
400	1.488×10^{-3}	8.40	2.13

B. $KClO_3$ + pDVB + $CoSO_4$

225	2.01×10^{-3}	2.86	1.05
250	1.91×10^{-3}	20.0	3.00

C. $KBrO_3$ + pDVB + $Al_2(SO_4)_3$

300	1.745×10^{-3}	0.526	-0.642
275	1.817×10^{-3}	0.100	-2.303

II F Catalysis and Inhibition of Solid-Solid Reactions

Impurities in solids undoubtedly affect their reactivity, sometimes to a marked degree, but impurity effects on the reaction between two solids have not been studied intensively because of the inherent experimental difficulties. The addition of substances to accelerate solid-solid reactions is common in practical applications but most of these additives are materials which reduce the eutectic temperature in the mixture and thus in most cases probably introduce a small amount of liquid phase.

In the present work the effect of additives on the solid-solid reaction between an oxidant and a substrate was studied. The effects of these additives must be viewed in the light of previous mechanisms proposed for reactions between solids. Thus, in order to arrive at an understanding of the effect of catalysts on the reaction it is necessary to clarify what the normal course of the reaction would be and what change, if any, the added substance will have on this mechanism.

The most comprehensive theories proposed for solid-solid reactions have been based on studies of the simplest systems available, viz., the thermal decomposition of solids.

Macdonald(34) interprets the thermal decomposition of silver oxalate as follows: the reaction starts from a fixed number of nuclei, which depends on the history of the sample. From there it spreads in two dimensions across the planes of the crystal. These planes of reaction may branch and they usually do so from the initiating spot on the edge or corner of the crystal, since this possesses considerable excess energy due to its special position on the crystal surface. When paraffin or certain other substances are adsorbed on the surface, however, this excess energy is removed. The reaction is thereby greatly retarded, and proceeds by the spontaneous generation of fresh planes at the edges of the spent reaction planes.

Prout and Tompkins[illegible] theory, based on the thermal decomposition of $KMnO_4$, is the most generally accepted mechanism for decompositions of solids. This theory stresses the importance of branching during reaction caused by the covering of the surface by product molecules and takes into account the effects of interference on the branching process. The formation of product molecules is thought to induce strain in the crystal, owing to molecular volume changes, producing cracks and thus forming fresh surfaces on which decomposition can occur.

This theory closely resembles that of nucleation of Garner and others(9-11) whereby reaction occurs in favourable regions, where the molecules exist in a state of comparatively higher energy levels, and therefore the activation energy will be lower. In general, the surface array of product molecules will have a different unit cell from that of the original substance and this sets up strains in the crystal surface which are relieved by the formation of cracks. At the mouths of these cracks the reaction will be enhanced by lattice imperfections and spread down these crevices into the crystal. Decomposition on these surfaces produces further strains and cracking, thus developing a type of chain branching process.

The mechanism proposed by Glasner and Weidenfeld(18) for the thermal decomposition of potassium perchlorate is based on a similar branching chain concept. The diffusion of oxygen after dislocation from the perchlorate ions is stated to be the rate limiting step.

All the above mechanisms are based on the original concepts of Schottky and of Frenkel(11, 19, 62) whereby movement of ions and electrons in solid ionic compounds is possible if there are deviations from the strict order of an ideal lattice. Reactions between solids require diffusion processes in the layers of the reaction products occurring by the movement of ions and electrons.

The Schottky concept, which probably applies to the present work, is of vacant anion and cation sites in the lattice. These vacancies can migrate through the lattice by a diffusion mechanism.

In a consideration of the mechanism of catalysis by a solid of a solid-solid reaction the following factors should be considered:

(1) Any impurity incorporated into the crystal lattice, will, as a rule, be unable to arrange itself in the original lattice structure of the pure substance. Hence it will give rise to lattice imperfections such as vacancies or excess ions or both.

(2) Ions move from normal lattice positions into adjacent vacant sites eliminating the original holes and creating new holes. Similarly excess ions, being also lattice defects, give rise to ionic interchanges in the structure.

(3) The electronic structure of a solid as well as its ionic properties are connected with its catalytic activity.

(4) During the decomposition of a substance, products may be formed which may catalyze or inhibit the further reaction.

The absence of autocatalysis in the reaction between $KClO_4$ and pDVB is shown by the reaction curve having no initiation period, i.e. it is not sigmoidal. Thus the KCl formed in the reaction does not catalyze the further reaction of $KClO_4$. The addition of KCl also does not change the rate of reaction from that of the uncatalyzed reaction. In the thermal decomposition of $KClO_4$, Glasner and Weidenfeld(18) found that pure perchlorate evolved oxygen according to a sigmoid reaction curve and that added chloride reduced or eliminated the induction period.

Glasner and Weidenfeld also investigated the influence of KCl derived from a decomposition of $KClO_4$ as compared with heat-treated KCl and ordinary KCl on the thermal decomposition of potassium chlorate. The various species of KCl affected the course of the reaction, the first two types increasing the rate of formation of perchlorate considerably. They attribute this effect to the ability of the treated KCl to absorb oxygen from the decomposing $KClO_3$ and to form perchlorate. In the case of perchlorate formation from KCl which originated from perchlorate the phenomenon is suggested to be a "memory" effect. That is to say, a substance such as KCl, obtained from $KClO_4$ by removal of oxygen atoms "remembers" its original crystal structure and reacts as a reducing agent in contact with substances which provide oxygen for filling out its lattice vacancies. The same "memory effect' was postulated by Weyl and Förland(64) for Ti_2O_3 formed by decomposition of TiO_2 and for BaO formed from the decomposition of BaO_2 etc., where the Ti_2O_3 and the BaO are much more reactive towards oxygen if they have been formed by the decomposition of the higher oxide, i.e., they "remember" their previous structure and return to it easily.

In the present work the reaction between $KClO_3$ or $KClO_4$ and pDVB sometimes went to 100% KCl in the presence of a suitable catalyst. This shows that the transfer of oxygen from one part of the reacting mass to another, i.e. to the pDVB must be rather facile and the product KCl formed is not an effective barrier. This may be due to a memory effect of the product lattice allowing easy diffusion of oxygen. On the other hand, KCl is not a catalyst, as shown by experiments using initially added KCl up to 2%. Therefore a balancing of two opposing effects, i.e. a "chemical" catalysis by KCl as opposed to a "physical" inhibition by the same substance as a barrier, is not tenable.

A possible mechanism that explains the phenomenon of catalysis or inhibition in a solid-solid reaction can be inferred from the work of Marshall, Enright and Weyl(35) on the influence of lattice defects in changing the rate of material transport through the bulk of a crystal. To demonstrate this influence they chose zinc oxide as the parent crystal and introduced various ions into the zinc oxide lattice. When Ga^{3+} ions were used the formation of Zn^+ ions takes place without producing anion vacancies. The crystal thus formed has the same electronic properties as the defective crystal which contains anion vacancies, but its lattice sites remain occupied. As a result, the material transport which leads to recrystellization and sintering is delayed.

They found that the same reasoning is valid for the reverse process, namely, causing the rate of material transport to be increased. For example, the substitution of Li^+ ions for Zn^{2+} ions in the zinc oxide lattice causes the electronic conductivity to be decreased sharply and the rate of material transport to be increased. Li^+ ions occupying normal Zn^{2+} ion sites in the lattice required that some ions leave the structure in order to maintain electrical neutrality. Thus the number of anion vacancies increases and consequently the rate of material transport also increases.

Such a concept may explain some but not all of the effects of the catalysts used in the oxidant-pDVB reactions in the present work. The catalytic effect of highly dissociated substances could be due to the relative ease with which they enter the oxidant crystal lattice and affect the diffusion of the reacting particles. Dissociable substances which neither inhibited nor catalyzed were of the same structural type as the oxidant, e.g., KBr, KCl, KI. Other substances which neither catalyzed nor inhibited were those which were very unlikely to enter the crystal lattice of the oxidant under the experimental conditions, namely the metal powders and water-insoluble oxides.

Some of the inhibition effects of various substances may be due to pure physical blocking of diffusion. It is possible that some of the soluble oxides are easily incorporated into the oxidant lattice during the "wetting" step of the tablet preparation. This effect would not operate with water insoluble or very slightly soluble compounds.

The only other obvious differentiation between catalysts and inhibitors occurred with acid and basic substances. It is very likely that the same mechanism of crystal lattice infiltration takes place and that the subsequent effects are due to the specific influence of acids and bases as electrophilic and nucleophilic substances on the potentially reactable particles. It would be difficult to ascertain which mechanism of acid catalysis applies in such a complex mechanism as studied here, although some clues may be found in other work:

According to a series of papers by Lyons(33) the photoconductivity of various organic solids involves the movement of negative oxygen ions, O^- or O_2^- on the surface of these solids. It is conceivable that in the present case the actual material transport of oxygen also takes place in the form of O^- or O_2^- ions. If this is the case, the presence of Lewis acids may catalyze the oxidation by the formation of intermediates, e.g.

$$O_n^- + A \rightleftharpoons \left[AO_n\right]^- \xrightarrow{\text{pDVB}} \text{products}$$

The inhibition by basic (nucleophilic) substances does not necessarily involve the converse of this mechanism, although it is reasonable to assume that nucleophilic substances would form an effective electrostatic barrier to the movement of negatively charged ions.

A further possibility, the decomposition of perchlorates by acids with the formation of chlorine peroxide or perchloric acid, which are more reactive than perchlorates or chlorates, is ruled out by the fact that in the absence of p-DVB, mixtures of perchlorate or chlorate and the acidic catalysts were quite stable. The formation of either chlorine peroxide or perchloric acid would necessarily lead to oxygen and/or chlorine evolution at the temperatures at which our experiments were conducted, whereas the experiments showed unequivocally that no such decomposition took place.

Inhibition or negative catalysis is a phenomenon quite common in reactions in solution. Most theories which were advanced to explain it proceed on the basis that the inhibitor intervenes at some stage in the original course of the reaction, i.e., it traps one of the necessary reactive intermediates, making the reaction more difficult or impracticable. From the standpoint of the theory of reactions taking place by intermediate stages it can be assumed that some particular link in the reaction, whether it be a catalyst, or one of the reactants, or an intermediate, is wholly or partly removed by the formation of an inert compound(54). In the case of reactions which occur without the aid of catalysts the simplest assumption is that the reactive form or an active intermediate state of one of the reactants or of an intermediate compound is removed by the negative catalyst.

The solid-solid reaction between pDVB and the oxidant has been postulated above to occur between pDVB and molecular or atomic or negatively charged oxygen, promoted by ion vacancies and crystal strains and cracks. The presence of inhibitors may also influence the reaction by deactivation of the reactive and mobile form of oxygen. Thus if a metal were the added substance it might either strongly absorb the oxygen on its surface or form a difficultly reducible oxide. Even if higher oxides were formed in some cases these may still be unreactive enough to inhibit the reaction.

It is impossible to assign a unified hypothesis for catalysis and inhibition on the basis of our experiments. Rather, it is probable that several mechanisms exist, for both catalysis and inhibition, and these may be physical and chemical in nature with various added substances. The above mentioned generalizations may be valid for a restricted group of cases only.

EXPERIMENTAL

(1) Materials used:

The oxidizing agents ($KClO_4$, $KClO_3$, $KBrO_3$, KIO_3, KNO_3, SeO_2 and chloranil) and the various additives used (V_2O_5, $Fe_2(SO_4)_3$, LiCl, Cr_2O_3, $Al_2(SO_4)_3$, MnO_2, etc.) were of the highest available analytical grades.

The organic substrates used were generally purified commercial compounds (chrysene, anthracene, oxamide, dicyclohexylamine). Cyclohexylcarboxylic acid was prepared by Grignard reaction of cyclohexylchloride(13).

Preparation of polymers:

Poly-divinylbenzene-ithylstipene copolymer, ("pDVB"), was prepared by polymerization of a commercial mixture (Light & Co.) consisting of about 40% divinylbenzene and 60% ethyl styrene. This was heated with 0.4% of benzoylperoxide for 24 hours at 60°C, for another 24 hours at 70°C and finally for 24 hours at 90°C. The resulting light yellow, brittle copolymer decomposed without melting at about 450-470°C.

Cinnamalfluorene was polymerized at 240-250°C in a sealed tube for three days(60, 65). After extraction of the benzene-soluble fraction, the residue (10% yield) melted at 360°C.

Decacyclene(51) was prepared from acenaphthene; it melted above 360°C.

Polymers were also prepared from indene, vinyl naphthalene and from styrene-DVB mixtures, but were unsatisfactory for our purposes.

(2) Preparation of samples

The reactants and the catalysts were ground finely and sieved. The material passing the 100 mesh sieve (U.S. Standard Sieves) and retained by the 200 mesh sieve was used in nearly all the experiments. The oxidant and substrate in the chosen ratio were thoroughly mixed and then further mixed with a quantity of catalyst in a fixed catalyst to oxidant ratio. Pellets of 10 mm diameter and weighing between 150 and 250 mg were pressed from the slightly wetted mixtures at 6000 lb/sq in. The pellets were dried at 120° for about 24 hours, cooled in a desiccator, weighed and placed in glass tubes which were evacuated to approximately 10^{-4} mm and sealed <u>in situ</u>.

In the preliminary experiments, tablets were of a larger size (15 mm diameter, 1 gm weight) and heated in tubes sealed at atmospheric pressure.

The tablets were in nearly all cases quite stable mechanically, especially after drying.

(3) Apparatus

Pellets were pressed in a three-part steel die of 10 mm inside diameter under a Carver Laboratory Press.

A mercury diffusion pump was used for evacuation and degassing of the samples.

Reactions were carried out in an electrically heated furnace regulated by a Fisher Pyrometer Controller to $\pm 5^{\circ}$C. The furnace had a capacity of nine samples placed in nine holes drilled in a circle in a brass block which was surrounded by the heating element. The temperature variation between the holes was less than 2°C. The glass tubes containing the samples were of 10.5 mm inside diameter and about 11 cm in length. These were placed simultaneously in the furnace in thin-walled brass tubes with wire handles. The brass tubes were slightly larger than the glass ampoules and slightly smaller than the furnace holes. A lid, insulated in the same manner as the furnace, covered the top of the furnace and the whole apparatus was surrounded by a metal shield. Adequate safety precautions were observed throughout the work.

Apparatus for determining ignition temperatures

Ignition temperatures were determined by dropping samples into open pre-heated test-tubes in the same furnace as described above and measuring the ignition time with a stopwatch. The samples were observed in a conveniently-placed mirror.

(4) Kinetic runs

The pellets in the evacuated and sealed tubes were placed in the pre-heated furnace at the desired temperature of reaction and removed after the desired time interval, allowed to cool, opened and analysed to determine the percentage reaction. In this way the percentage reaction of a particular mixture was found for various periods of heating, generally from 1 to 24 hours and the nine results for each run were plotted time vs. % reaction (see Table 24 for typical results).

$KClO_4$ and $KClO_3$ oxidations were followed analytically by the Volhard method of chloride analysis. $KBrO_3$ and KIO_3 oxidations were analysed iodometrically by determining the amount of $KBrO_3$ or KIO_3 in the residue.

Other experiments were carried out to determine the decomposition of the substrate without oxidants or catalysts, and without catalysts; the decomposition of the oxidant with the catalyst (absence of substrate); the analysis of the organic products of the catalyzed oxidation of the substrate; the decomposition of the oxidant without catalyst or substrate. These experiments were carried out under identical conditions in the processing of the samples.

In the oxidation of polycyclic compounds the organic products were analysed spectrophotometrically and the inorganic ones volumetrically to see whether changes in the organic substrate corresponded to changes in the inorganic or organic oxidant.

(5) Calculations

(a) Kinetics

The percentage of reaction was calculated from the amount of halide formed in the decomposition of the oxidant. The percentages of reaction were plotted against time of reaction and the values of t for percentages of reaction of 5, 10 .... 60% tabulated. These values of t were used to obtain the value of the rate constant, k, from the tabulated values of kt corresponding to the appropriate empirical rate equation.

The dimension of the rate constant is therefore $\left[\text{time}^{-1}\right]$ since the concentration terms being mole per mole are dimensionless.

Values of kt were calculated for empirical rate equations of the general form:

$$dx/dt = k(a-x)/x^n$$

for various values of n. The above differential equation was expanded into the geometrical series:

$$kdt = \frac{x^n}{a}\left[1 + \frac{x}{a} + \left(\frac{x}{a}\right)^2 + \left(\frac{x}{a}\right)^3 + \dots\right]dx$$

and integrated for various values of n.

(b) Activation Energy

Activation energy was calculated from the plot of $\frac{1}{T_{abs}}$ vs ln k from the Arrhenius equation:

$$\ln k = \ln A - {}^{E}/_{RT}$$

which gives a line of slope ${}^{E}/_{R}$ whence E can be determined.

TABLE 24

Typical Kinetic Runs With Mixtures of Oxidant - pDVB - Added Substance

% Reaction

Run No.	Temp.	W Oxidant / W pDVB	W Catalyst / W Oxidant	Time (hrs.) →	0.5	1	2	3	4	5	6	7	8	9	10	15	16	23	24	25	28.5	40
71	350°	$5KClO_4$	$0.028Al_2(SO_4)_3$			10.5	20.5	16.3		21.9			29.7		36.7		44.8		47.4			
34	"	"	0.024Al			2.3	5.1		6.9		9.4			9.0			15.9	17.8				21.1
102	"	"	$0.028CaCO_3$			0.8		3.7		4.7		6.2			7.8		10.7		12.2		13.2	
42	"	"	$0.028Fe_2(SO_4)_3$			12.8		20.9		30.9		32.7		36.6			44.5		46.6			
C 44a	225°	$5KClO_3$	$0.028Al_2(SO_4)_3$		0.2	1.7	2.8	3.8	5.2	10.1	15.4		16.7				25.2					
C 45a	"	"	$0.028Fe_2(SO_4)_3$		0.9	2.5	5.5	9.2	12.3	14.4	18.1		24.3				48.8					
B 20	300°	$5KBrO_3$	$0.028Al_2(SO_4)_3$			17.3	13.2	28.8	31.5		35.4	41.6		51.8			52.7		57.4			
B 11	"	"	$0.028V_2O_5$			8.4	17.0	18.5	26.9	24.3			31.0			41.8			50.9			
I 20	325°	$10KIO_3$	$0.028NH_4Br$			4.8	11.5	11.9		12.2		17.5		17.1			22.0		25.6			
I 16	"	"	$0.028MnSO_4$			13.8	19.9		23.3		28.4			38.1			37.4			47.5		

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