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The kinetic compensation effect for the thermal decomposition of some polymers

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Abstract

The kinetic compensation effect was investigated for a great variety of polymers, showing its existence for a homogeneous solid state decomposition.

INTRODUCTION

The kinetic compensation effect (KCE) was first developed in catalysis studies to account for the fact that differing treatments of a catalyst resulted in a change in the calculated activation energy but with no corresponding change in the reaction velocity, the rate of the reaction remaining constant. To explain this, it was suggested that the pre-exponential factor A varied with the activation energy E in accordance with the equation

$$\log A = aE_a + b$$

This relationship between the two kinetic parameters was termed the "kinetic compensation effect".

The effect has since been observed in many types of reaction, both organic and inorganic, in a number of different areas including hydrolysis, oxidation and thermal decomposition. Although it has been the subject of much investigation over recent years, it has still to be satisfactorily explained and there are several conflicting theories regarding the effect. Opinions are divided over whether it is a true effect arising from some physical or chemical process of the reaction or an apparent effect due to an artefact.

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Dedicated to Professor Joseph H. Flynn in honour of his 70th birthday.

CATALYSIS STUDIES

The first observation of the KCE was by Constable [1] when investigating the dehydrogenation of ethanol on copper catalysts prepared by the reduction of copper oxide at different temperatures. At first it was thought to be a special case but observation of the effect over a far wider range of activation energies and pre-exponential factors led to the opinion that it was a general phenomenon. Early observations of the effect were with variation of the catalyst and a fixed substrate [2,3], but later examples appeared when the effect was observed by using different substrates with the same catalyst [4]. Kera and Negoro [5] studied the thermal decomposition of alcohols over alkali vanadates and found a good linear relationship between log A and E_a for each alcohol decomposition for a series of alkali vanadates. They attributed the effect to a proportionality between the entropy of activation and the inner frictional rotation of the alkyl groups in the activated alcohol molecule.

Rhim et al. [6] have demonstrated the appearance of the KCE in the acid-catalysed hydrolysis of disaccharides. Three disaccharides, sucrose, maltose and lactose, were studied and the degree of hydrolysis measured as a function of the acid concentration. Although a large variation was found in the kinetic parameters of activation energy and pre-exponential factor, the values fitted a linear compensation relationship with values for the compensation parameters a and b of 0.295 and -2.317 mol kJ^{-1} respectively.

THERMAL DECOMPOSITION

The applicability of the KCE to thermal decomposition reactions was not appreciated until the early seventies when Gallagher and Johnson [7] and Zsako and Arz [8] investigated the kinetics of the thermal decomposition of calcium carbonate. When the decomposition took place in oxygen,

TABLE 1

Compensation parameters of various thermal decomposition reactions

Compound	a (mol kJ^{-1})	b	r
$CuCl_2 \cdot 2H_2O$	0.1539	−3.4806	0.9996
$CaC_2O_4 \cdot H_2O$	0.1078	−1.8163	0.9999
	0.1094	−1.9581	0.9999
	0.1245	−2.4629	0.9997
	0.1272	−2.7559	0.9999
ZnOH	0.13	−2.33	
	0.14	−4.29	

TABLE 2

Percentage conversion as a function of temperature for four heating rates (β)

log $1/\beta$	Temperature (°C) for percentage conversion								
	10%	20%	30%	40%	50%	60%	70%	80%	90%
Polyethyleneterephthalate–2.4% carrier									
0.0000	345	360	368	374	378	382	387	392	400
−0.1761	340	367	374	381	387	391	397	407	450
−0.3010	367	378	383	392	397	402	408	420	472
−0.6021	381	389	399	402	406	413	419	430	494
Polyethyleneterephthalate–8% aluminium									
0.0000	349	361	371	377	382	387	395	408	449
−0.1761	354	368	375	381	386	400	407	426	478
−0.3010	361	376	380	387	396	400	403	429	472
−0.6021	376	387	392	398	403	409	417	441	497
Pure polyvinylchloride									
0.0000	231	244	253	258	264	272	306	416	467
−0.1761	238	249	257	262	270	278	312	436	475
−0.3010	248	261	268	274	281	291	356	443	499
−0.6021	266	280	285	293	300	308	322	429	510
Polyvinylchloride–2.4% carrier									
0.0000	236	247	253	259	265	274	326	420	468
−0.1761	240	255	263	270	275	282	326	425	479
−0.3010	254	260	267	274	281	286	369	438	494
−0.6021	266	275	286	294	300	307	327	436	520
Polypropylene–2.4% carrier									
0.0000	261	286	306	317	327	333	341	355	371
−0.1761	265	285	302	316	326	333	341	355	381
−0.3010	277	297	309	318	331	341	352	363	386
−0.6021	306	333	353	373	388	396	404	413	425
Polypropylene–8% aluminium									
0.0000	238	371	385	303	316	322	328	332	345
−0.1761	240	265	284	302	317	326	335	346	377
−0.3010	251	274	295	310	322	331	340	347	354
−0.6021	279	301	323	340	355	367	379	390	407
Pure HDPE									
0.0000	349	364	373	380	386	394	402	410	419
−0.1761	360	376	385	392	397	408	416	422	428
−0.3010	375	385	395	403	410	419	423	428	434
−0.6021	353	382	401	415	429	436	445	453	461
HDPE–2.4% carrier									
0.0000	369	377	385	396	403	411	414	420	429
−0.1761	367	381	389	395	401	406	412	421	434
−0.3010	377	390	398	405	414	421	427	433	440
−0.6021	387	407	425	433	441	446	453	457	463
Pure nylon 6									
0.0000	335	360	375	384	396	401	407	418	453
−0.1761	351	372	381	390	397	401	409	420	463
−0.3010	357	374	387	396	402	410	417	428	472
−0.6021	373	393	410	418	427	432	438	445	482

TABLE 2 (continued)

log $1/\beta$	Temperature (°C) for percentage conversion								
	10%	20%	30%	40%	50%	60%	70%	80%	90%
(Nylon 6)–2.4% carrier									
0.0000	342	361	372	382	391	397	405	429	457
−0.1761	340	362	375	383	391	399	405	418	441
−0.3010	356	371	383	394	401	407	414	428	471
−0.6021	368	390	402	410	419	424	431	438	478
(Nylon 6)–8% aluminium									
0.0000	339	361	372	386	394	400	410	418	467
−0.1761	344	364	376	383	391	398	405	417	445
−0.3010	352	372	383	393	400	407	414	424	450
−0.6021	371	395	407	414	425	431	436	441	452
Pure polyethyleneterephthalate									
0.0000	337	356	367	375	381	386	393	401	448
−0.1761	350	367	376	381	386	391	399	405	452
−0.3010	356	373	382	387	393	398	404	417	467
−0.6021	373	387	395	400	406	412	420	434	504
HDPE–8% aluminium									
0.0000	361	375	381	397	405	413	416	420	427
−0.1761	376	385	395	403	411	417	420	423	427
−0.3010	372	382	394	403	410	421	428	431	436
−0.6021	364	396	418	430	440	447	454	460	467
Pure LDPE									
0.0000	340	361	372	380	385	393	401	403	407
−0.1761	353	365	373	381	389	394	400	414	428
−0.3010	359	372	380	388	398	403	410	416	427
−0.6021	362	382	401	412	424	429	433	439	445
LDPE–2.4% carrier									
0.0000	356	362	372	378	382	389	397	409	418
−0.1761	354	367	376	381	387	394	400	405	426
−0.3010	365	375	382	391	400	405	411	416	423
−0.6021	357	387	408	417	428	434	438	444	448
LDPE–8% aluminium									
0.0000	363	371	379	390	395	400	405	412	417
−0.1761	346	372	380	389	397	407	415	420	424
−0.3010	380	390	399	408	414	420	425	430	436
−0.6021	365	385	400	410	420	427	436	441	448
Polyvinylchloride–8% aluminium									
0.0000	232	245	254	259	265	278	333	431	481
−0.1761	237	254	260	265	271	281	342	426	482
−0.3010	248	262	270	279	284	294	364	433	500
−0.6021	266	275	286	294	300	307	327	436	520

Gallagher and Johnson found that the kinetics of the reaction were dependent upon sample size and heating rate, and correlation was observed between the activation energy and the pre-exponential factor in accordance with the kinetic compensation law. On repeating the experiments in an atmosphere of carbon dioxide, the KCE was still observed, although the parameters *a* and *b* differed. The results obtained were: in O_2, $\log A = 0.278E_a - 5.98$, and in CO_2, $\log A = 0.175E_a - 2.95$.

Adonyi and Körösi [9] also investigated the decomposition of calcium carbonate and observed a KCE for particular sample weights at different heating rates. The compensation parameters they derived are shown, with the correlation coefficient *r* of the straight line.

Other thermal decomposition reactions studied include those of $CuCl_2 \cdot 2H_2O$, $CaC_2O_4 \cdot H_2O$ [10] and ZnOH [11]. All were found to exhibit a KCE and the compensation parameters obtained for the three reactions are shown in Table 1.

Although a large number of reactions have been investigated and shown to exhibit a KCE, the controversy over whether the effect has any chemical or physical significance has still to be resolved. One of the main opponents of the effect being “real” is Garn [12]. He believes that the effect arises from the form of the Arrhenius equation and claims that any experimental values showing a variance with temperature can be adjusted to approximate a straight line.

While agreeing with Garn that the kinetic parameters do not have the same physical significance in heterogeneous kinetics as in homogeneous kinetics owing to their dependence on variables other than temperature, Zsako [13] maintains that this merely results in a masking of the true effect rather than proving it is only an apparent effect. By the use of theoretical TG curves he demonstrates the characterisation of a reaction via the compensation parameters *a* and *b*, rather than the kinetic parameters. The results he obtains show that for a series of TG curves of a particular reaction, values of A and E_a vary for each individual TG curve, depending on procedural variables while the compensation parameters describing the reaction remain the same, suggesting that they are independent of procedural variables.

In the present work, we report data on the thermal decomposition of a range of polymeric materials, including composites. For decomposition within the organic medium, the reaction is homogeneous. The presence of an added carrier polymer and/or metal powder should not significantly affect the homogeneity of the reaction, although it may change heat transfer characteristics.

EXPERIMENTAL

Weight loss on heating was measured using a Stanton automatic thermobalance with varying heating rates. The data obtained for programmed runs were analysed to yield A and E, the pre-exponential factor and the activation energy, using an empirical relationship developed some years ago [14], assuming the reaction has an apparent order of unity.

TABLE 3

Compensation parameters for KCE in thermal degradation reactions of polymers

Polymer composite	*a* (mol kJ^{-1})	*b*	*r*
Polystyrene			
Pure	0.0958	−2.25	0.999
2.4% carrier	0.0902	−1.91	0.998
8% aluminium	0.0911	−1.88	0.999
LDPE			
Pure	0.0834	−1.89	1.000
2.4% carrier	0.0843	−2.01	0.999
8% aluminium	0.0856	−2.47	1.000
HDPE			
Pure	0.0863	−2.39	1.000
2.4% carrier	0.0815	−1.89	1.000
8% aluminium	0.0817	−1.93	0.999
Polypropylene			
Pure	0.0816	−1.09	0.998
2.4% carrier	0.0872	−1.58	0.996
8% aluminium	0.0879	−1.36	0.998
Nylon 6			
Pure	0.0744	−0.84	0.996
2.4% carrier	0.0824	−1.88	0.999
8% aluminium	0.0787	−1.36	1.000
PET			
Pure	0.0854	−2.22	1.000
2.4% carrier	0.0834	−1.85	0.999
8% aluminium	0.0876	−2.74	1.000
PVC			
Pure	0.0772	−0.38	0.930
2.4% carrier	0.0755	0.38	0.919
8% aluminium	0.0724	0.45	0.995

The polymers used were as indicated, with polyethylene as carrier material and with freshly prepared aluminium flake as the metal additive. Samples were prepared by milling the constituents and extruding the products.

RESULTS

The percentage change in mass as a function of temperature was obtained at four different heating rates and the results are shown in Table 2. Assuming that the apparent order of reaction is unity, the data were analysed for *A* and *E* using a methodology published some years ago. The values obtained were tested for the KCE and the resultant compensation parameters are shown in Table 3 along with the correction coefficient *r*. For each system given in the table, at least eight points were used and apart from measurements on PVC samples, an impressive correlation is obtained for the values of *a* and *b* which are close to those obtained for entirely different situations.

CONCLUSIONS

In this work involving a homogeneous solid state decomposition, it appears that the KCE applies. The question remains—is the effect real or an artefact? There is no theoretical justification for this relationship and we support Garn's thesis that it is an artefact. However, the fact remains that a widely diverse range of systems obeys the relationship such that the possibility of sample coincidence is virtually impossible. The phenomenon is worth further investigation because the occurrence of such a widespread artefact would seriously weaken the credibility of the basic data. An obvious weakness in the above analysis is the assumption of a unique value of unity for the apparent order of reaction. However, deviation from such a value is difficult to justify because no residue accrues from the thermal reaction and furthermore all the results obtained were independent of the initial mass of the test sample.

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