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Kinetic data computation from thermogravimetric curves of some aryliodine(III) dicarboxylates

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Abstract

Mass spectral and thermal studies of several aryliodine(III) dicarboxylates in a static air atmosphere have been carried out to determine their modes of decomposition. Fragmentation patterns are given and possible mechanisms are discussed. All compounds show similar thermograms and DTA profiles. Reaction orders were estimated by employing the Freeman–Carroll equation, and a kinetic analysis of the TG data was performed using the Coats–Redfern equation to determine the apparent activation energies and the pre-exponential factor of the Arrhenius equation.

INTRODUCTION

Aryliodine(III) dicarboxylates, $ArI(OCOR)_2$, constitute a class of organic polyvalent iodine compounds with interesting oxidative properties resembling closely those of lead tetraacetate [1,2]. Although no systematic studies have been carried out so far concerning relationships of structure and reactivity, these compounds are versatile reagents in several areas of organic synthesis; further, they are useful in analytical applications. In particular, phenyliodine(III) diacetate serves as a redox titrant for the determination of dithiocarbamates and dithiocarbonates [3], and some analogues have been used in several potentiometric titrations [4,5]; other types of determinations have involved various sulfur compounds [6–8], amines [9] and histidine [10].

The thermal decomposition of aryliodine(III) dicarboxylates has received considerable attention [1]. Two major pathways have been recognized, involving unimolecular decompositions by concurrent radical and het-

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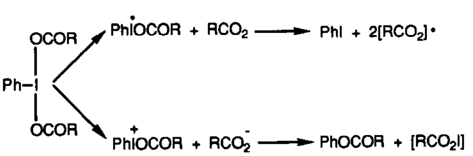


Scheme 1.

erolytic reactions as shown in Scheme 1. The homolytic path produces aroyloxy or acyloxy radicals which, on losing CO_2, either dimerize into R–R or are converted into esters RCOOR [11–14]. Kinetic and product studies [15] concerning the thermolysis of phenyliodine(III) dibenzoate in bromobenzene at 145.5°C indicated the reaction to be strictly first-order with a mean rate constant of $8.48 \times 10^{-5}\ s^{-1}$.

These detailed studies on the thermal decomposition of the title compounds in solution have not been paralleled by analogous studies in the solid state, with some exceptions of exploratory character. Thus, thermolysis of some $ArI(OCOMe)_2$ compounds followed the heterolytic pathway to give ArOCOMe [16], whereas $ArI(OCOAd\text{-}1)_1$ were converted homolytically via elimination of ArI and CO_2 into esters 1-Ad-COO-Ad-1 [17] (Ar = mesityl; Ad-1 = 1-adamantyl). In the case of some compounds having the general formula $PhI(O_2CCH_2OAr)_2$, their thermolysis afforded initially unstable products which were further transformed, mainly into $ArOCH_2CO_2CH_2OAr$ [18]. We report presently results concerning mass spectral and TG/DTA studies for several members of the series. Furthermore, the differential method using the Freeman–Carroll equation [19] and the integral method employing the Coats–Redfern equation [20] are used for the calculation of kinetic parameters from a non-isothermal kinetic study.

EXPERIMENTAL

Preparation of samples

Aryliodine(III) diacetates $XPhI(OCOMe)_2$ ($X = CH_3$, Cl, NO_2) were prepared by direct oxidation of the appropriate iodoarenes with 30% H_2O_2 in acetic anhydride [21]. The dibenzoates were obtained either from the diacetates by exchange [13] with benzoic acid or from iodosylbenzene and benzoic acid [22]. They were recrystallized from chloroform–petroleum ether.

Instruments

Mass spectra were run at 70 eV on an RMU-6L Hitachi Perkin–Elmer single focusing mass spectrometer, using direct probe insertion for the

TABLE 1

Main mass spectral peaks of some aryliodine(III) dicarboxylates

Compound	*m*/*z* (relative intensity)
PhI(OCOMe)$_2$	15 (52), 28 (14), 29 (32), 43 (22), 44 (32), 45 (57), 51 (32), 60 (82), 74 (21), 75 (11), 77 (95), 78 (9), 94 (14), 127 (45), 128 (11), 204 (100), 263 (4)
o-MePhI(OCOMe)$_2$	41 (26), 42 (18), 43 (67), 44 (83), 45 (52), 50 (18), 51 (30), 55 (20), 56 (10), 57 (16), 60 (24), 62 (11), 63 (21), 64 (9), 65 (38), 67 (6), 69 (29), 70 (7), 71 (8), 73 (7), 77 (9), 83 (6), 84 (8), 85 (6), 89 (22), 90 (15), 91 (100), 92 (10), 98 (6), 105 (7), 127 (9), 218 (82), 219 (7), 277 (21)
m-MePhI(OCOMe)$_2$	41 (4), 42 (3), 43 (20), 44 (10), 45 (16), 50 (6), 51 (7), 60 (12), 62 (6), 63 (12), 64 (4), 65 (30), 89 (12), 90 (6), 91 (80), 92 (7), 127 (5), 218 (100), 219 (8), 277 (10)
o-ClPhI(OCOMe)$_2$	43 (4), 44 (12), 49 (5), 50 (29), 51 (8), 73 (6), 74 (17), 75 (48), 76 (13), 85 (5), 99 (3), 111 (59), 112 (6), 113 (20), 119 (4), 127 (13), 238 (100), 239 (7), 240 (32)
m-ClPhI(OCOMe)$_2$	41 (5), 42 (14), 43 (92), 44 (32), 45 (83), 49 (14), 50 (94), 51 (28), 60 (62), 61 (9), 73 (14), 74 (45), 75 (100), 76 (28), 85 (7), 111 (74), 112 (7), 113 (25), 119 (5), 127 (7), 238 (78), 239 (6), 240 (28)
m-NO$_2$PhI(OCOMe)$_2$	28 (8), 30 (15), 37 (8), 38 (10), 46 (4), 49 (6), 50 (71), 51 (7), 63 (10), 64 (10), 73 (7), 74 (37), 75 (36), 76 (96), 77 (11), 92 (18), 127 (16), 191 (8), 203 (81), 204 (8), 249 (100), 250 (15)
o-MePhI(OCOPh)$_2$	44 (46), 50 (15), 51 (22), 52 (9), 63 (10), 65 (23), 74 (5), 76 (5), 77 (36), 78 (35), 89 (10), 90 (11), 92 (7), 105 (43), 106 (5), 127 (8), 128 (5), 154 (18), 168 (12), 204 (10), 212 (13), 218 (100), 219 (10), 254 (5), 294 (3), 339 (5)

samples. Probe temperature was in the range 140–180°C and chamber temperature was between 100 and 110°C. The ion source used was a T-2p model. The TG/DTA curves were obtained on a Rigaku–Denki model 8076-D1 thermal analyser. Samples were heated in platinum crucibles, using α-Al$_2$O$_3$ as a reference compound, in a static air atmosphere within the temperature range 25–1000 ° C. The heating rate was 5°C min^{-1}, and the recording paper rate was set at 2.5 mm min^{-1}. The sample sizes ranged in mass from 12 to 17 mg.

RESULTS AND DISCUSSION

Mass spectra

In all mass spectra recorded no molecular ion peaks (M$^{+\cdot}$) are detected, in accordance with the known enhanced thermal lability of aryliodine(III) dicarboxylates [22–24]; ions of both carboxylic or benzoic acids and iodobenzenes are predominant. The main mass spectral peaks of the compounds studied are given in Table 1, and a general schematic represen-

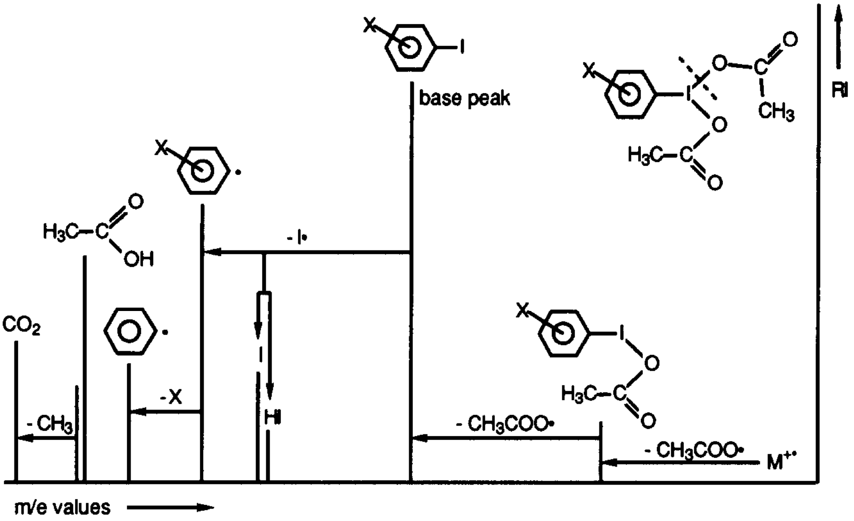


Fig. 1. Schematic representation of general fragmentation of substituted phenyliodine(III) diacetates (charges are omitted).

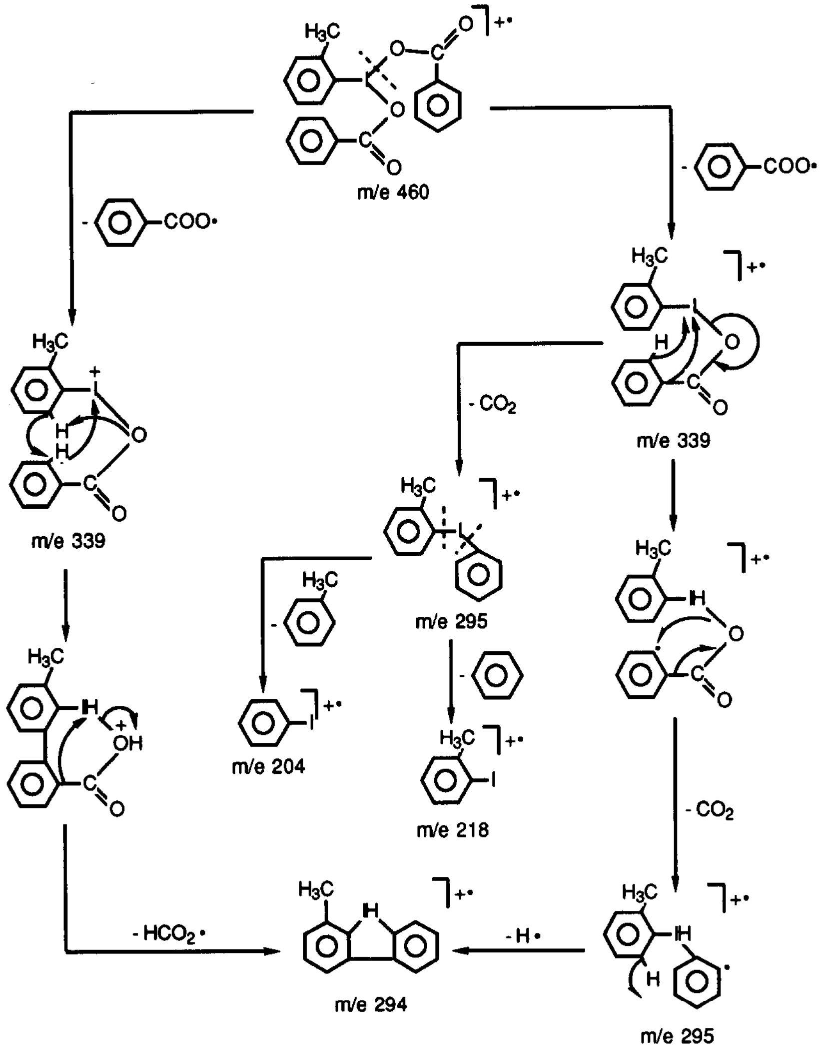
tation including the main fragmentation processes for $XPhI(OCOMe)_2$ appears in bar-graph form in Fig. 1.

The most important higher mass number ion in all compounds corresponds to the general formula $[ArIOCOR]^{+\cdot}$, and may be regarded as a direct fragment of the molecular ion, resulting after the rupture of one I–O bond. This ion, especially when an aryl moiety [22], undergoes several rearrangements involving expulsion of carbon dioxide or iodine, because of the general tendency of polyvalent iodine to acquire a more stable electronic configuration. Accordingly, elimination of carbon dioxide leads to the formation of iodonium compounds and then to iodoarenes, whereas esters are formed upon elimination of iodine, probably thermally. A simplified picture of the main fragmentation pathways for *o*-$MePhI(OCOPh)_2$ is presented in Scheme 2. It is worth noting that in all benzoates a dibenziodolium ion (at m/e 294 for this compound) is present.

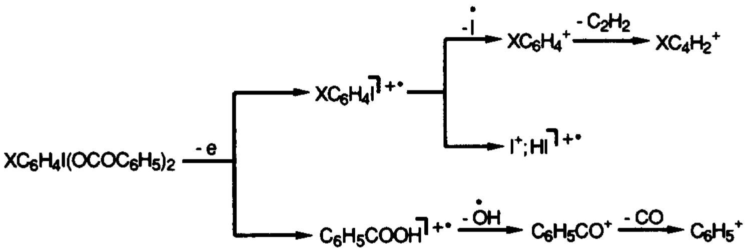
The most intense peaks of each spectrum are those corresponding to carboxylic or benzoic acids and iodobenzenes. These main daughter ions are further fragmented following well-known pathways, as shown in Scheme 3.

Thermal behavior

The thermal curves obtained for most of the compounds are very similar in character. Typical thermoanalytical curves are presented in Fig. 2. Aryliodine(III) dicarboxylates decompose in three nearly overlapping stages in a static air atmosphere. Decomposition is completed by about 900 °C,



Scheme 2.



Scheme 3.

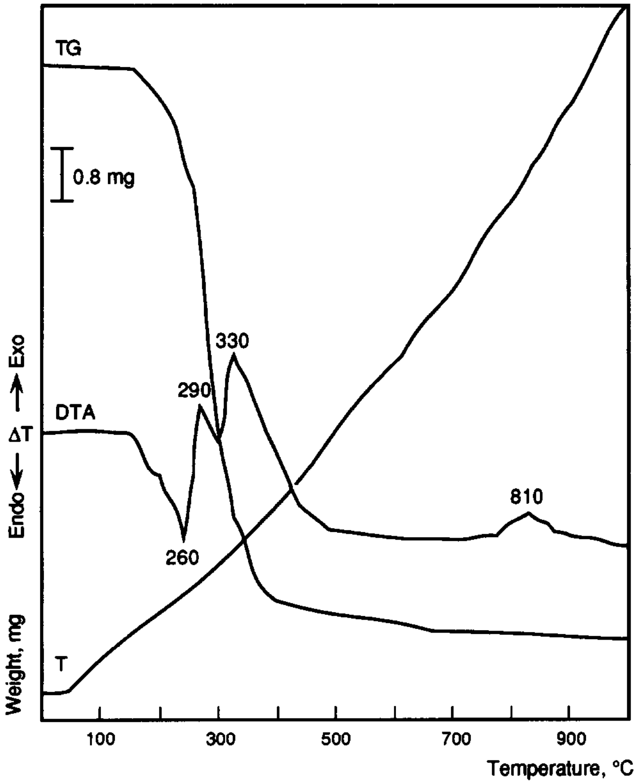


Fig. 2. Thermoanalytical curves of *m*-MePhI(OCOMe)$_2$ in air.

with 100% weight loss. The DTA curve shapes indicate that, apart from the endothermic effect corresponding to melting, the three degradation stages are accompanied by exothermic effects. The temperature ranges determined, percentage weight losses and thermal effects accompanying the decomposition reactions are given in Table 2.

Scheme 4 shows the proposed stages of the thermal degradation of ArI(OCOR)$_2$. The theoretical weight losses are consistent with the observed ones in the particular transition stages; the intermediates are unstable and undergo further rapid decomposition. In general, decomposition begins between 110 and 150°C, followed by a rapid weight loss of about 35%. This is a two-stage reaction which leads to iodobenzene through a consecutive cleavage of the two I–O bonds and the elimination of acetoxy groups. Thus, the first event in either electron-impact fragmentation or thermal degradation seems to be the elimination of an RCOO group. The proposed model of decomposition is speculative, because there is no possibility of isolating an intermediate between the first and second

$$\mathrm{XPhI(OCOR)_2} \xrightarrow{-\mathrm{RCO_2}} \{\mathrm{XPhIOCOR}\} \xrightarrow{-\mathrm{RCO_2}} \{\mathrm{XPhI}\} \xrightarrow{\mathrm{O_2}} \text{gases}$$

Scheme 4.

TABLE 2

Thermoanalytical results for aryliodine(III) dicarboxylates in static air

Compound	DTA		Step	Temperature range (°C)	Weight loss (%)	Assignment	Weight loss calc. (%)
	endo(−)	exo(+)					
$PhI(OCOMe)_2$	280	320, 360	1	130–400	35.8	$2MeCO_2$	36.67
		700br	2	400–900	64.2	PhI	63.33
o-$MePhI(OCOMe)_2$	250	280, 320	1	140–400	34.6	$2MeCO_2$	35.14
		760br	2	400–900	65.4	MePhI	64.86
m-$MePhI(OCOMe)_2$	260	290	1a	110–260	18.0	$MeCO_2$	17.57
		330	1b	260–400	17.6	$MeCO_2$	17.57
		810	2	400–900	64.4	MePhI	64.86
p-$MePhI(OCOMe)_2$	200	280	1a	150–280	19.6	$MeCO_2$	17.57
		308	1b	280–340	18.2	$MeCO_2$	17.57
		650br	2	340–700	62.2	MePhI	64.86
o-$ClPhI(OCOMe)_2$	240	260	1	140–255	18.8	$MeCO_2$	16.56
		290, 360	2	255–700	81.2	$MeCO_2$ +ClPhI	83.44
m-$ClPhI(OCOMe)_2$	270	305	1	100–240	16.6	$MeCO_2$	16.56
		335, 500	2	240–700	83.4	$MeCO_2$ +ClPhI	83.44
m-$NO_2PhI(OCOMe)_2$	55	360	1	145–330	48.2	$MeCO_2I$	50.65
		800	2	330–900	51.8	$MeCO_2$ $+PhNO_2$	49.35
o-$MePhI(OCOPh)_2$	240	320, 640	1	110–690	51.9	$2PhCO_2$	52.62
		720	2	690–740	48.1	MePhI	47.38

stages of degradation. Evidence for a two-stage reaction comes strictly from the DTA and TG curves. Further thermal degradation at about 400°C seems to be a one-stage process resulting from the combustion of iodobenzene.

Decomposition kinetics

For the first stage of decomposition involving elimination of an acetoxy group and formation of the unstable {XPhIOCOR} intermediate, the following kinetic parameters were calculated using the method of Coats and Redfern [20]: activation energy E^*, and pre-exponential factor Z.

The activation energy of thermal decomposition can be explained in terms of the probability that a molecule will possess energy in excess of an amount E^* per mole at temperature T, and is related to the Boltzmann factor $e^{-E^*/RT}$, where R is the molar gas constant. The reaction rate will clearly be dependent on the product of Z and $e^{-E^{*}/RT}$, where Z is the frequency factor representing the total frequency encounters between two reactant molecules, irrespective of whether they possess sufficient energy or not [20,25]. Thus, the decomposition equation for a first order reaction, i.e., when $n = 1$, of the type $A(s) \rightarrow B(s) + C(g)$ is

$$-\log\left[\frac{-\ln(1-\alpha)}{T^2}\right] = Z\ e^{-E^{*}/RT} \tag{1}$$

where α is the degree of decomposition, and

$$\log\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = Z\ e^{-E^{*}/RT} \tag{2}$$

when the order of reaction $n \neq 1$. On the other hand, the reaction order may be determined by employing the Freeman–Carroll equation [19] in the form

$$\frac{\Delta \log(\mathrm{d}w/\mathrm{d}t)}{\Delta \log w_r} = \frac{(-E^{*}/2.303R)\ \Delta(T^{-1})}{\Delta \log w_r} + n \tag{3}$$

where w_r = total weight loss at temperature T or time t. Details concerning the calculation procedure are given in previous papers [26–28].

The near unity values of the order of reaction derived from the above analysis of TG data show that first-order kinetics are applicable in all cases.

TABLE 3

Kinetic data for some aryliodine(III) diacetates

Compound	Parameter	Value	
		From Freeman–Carroll equation	From Coats–Redfern equation
m-MePhI(OCOMe)$_2$	E^{*} (kJ mol^{-1})	50.7	56.9
	Z (s^{-1})	1.05×10^{3}	4.37×10^{3}
	r	0.988	0.986
p-MePhI(OCOMe)$_2$	E^{*} (kJ mol^{-1})	60.1	67.1
	Z (s^{-1})	3.36×10^{3}	1.50×10^{4}
	r	0.994	0.989
o-ClPhI(OCOMe)$_2$	E^{*} (kJ mol^{-1})	64.8	68.9
	Z (s^{-1})	1.87×10^{4}	3.84×10^{4}
	r	0.990	0.993
m-ClPhI(OCOMe)$_2$	E^{*} (kJ mol^{-1})	53.0	54.7
	Z (s^{-1})	2.15×10^{3}	2.65×10^{3}
	r	0.987	0.996

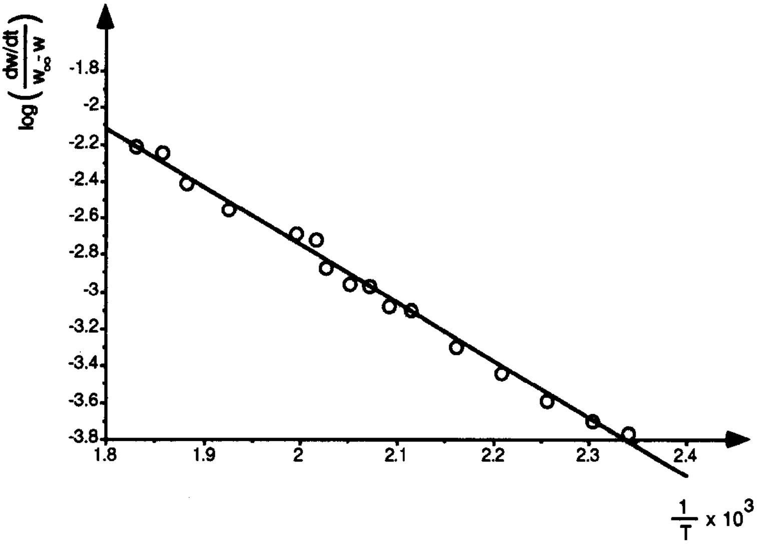


Fig. 3. Freeman–Carroll (modified) plot for *p*-MePhI(OCOMe)$_2$.

Therefore, by combining the usual first-order rate law expression with the Arrhenius equation [29], we get

$$\log\left(\frac{\mathrm{d}w/\mathrm{d}t}{w_\infty - w}\right) = \frac{-E^*}{2.303RT} + \log Z \tag{4}$$

where w_∞ = mass loss at the completion of the reaction, and w = mass loss

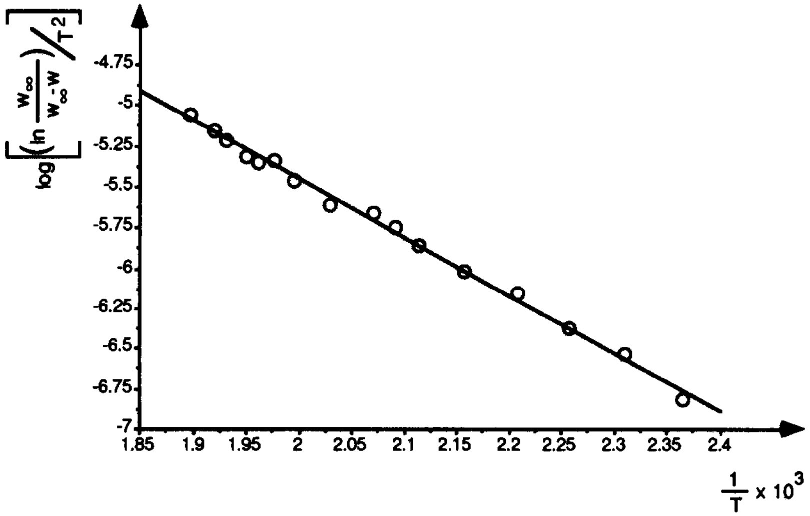


Fig. 4. Coats–Redfern plot for *o*-ClPhI(OCOMe)$_2$.

up to time t. Moreover, for first-order processes, eqn. (1) may be written in the form

$$\log \frac{2.303 \log\left(\frac{w_\infty}{w_\infty - w}\right)}{T^2} = \log \frac{ZR}{\Phi E^*}\left[1 - \frac{2RT}{E^*}\right] - \frac{E^*}{2.303RT} \tag{5}$$

where Φ is the rate of heating.

The kinetic parameters obtained by the application of eqns. (4) and (5) to the thermoanalytical data are summarized in Table 3. Typical curves are given in Figs. 3 and 4. All linear plots were evaluated by a regression analysis, and the corresponding correlation coefficients (r) were calculated. It follows from the calculated kinetic parameters that the pyrolysis of aryliodine(III) dicarboxylates is a low energy process, which is confirmed by the low activation energies.

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