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Thermogravimetric study of starch derivatives with amine/ammonium ion-exchanging groups in oxidative environment

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Abstract

The amine/ammonium materials were prepared by cross-linking of starch (S) with epichlorohydrin (E → SE) in the presence of ammonia (A → SEA) or choline ($C \rightarrow SEC{-}HO^-$) or with 1,3-bis-(3-chloro-2-hydroxypropyl)imidazolium hydrogensulphate (BCHIHS → $SHI{-}HO^-$) and transfered into the acid/salt forms with HCl (SEA–HCl, $SEC{-}Cl^-$, or $SHI{-}Cl^-$), H_2SO_4 ($SEA{-}H_2SO_4$, $SEC{-}HSO_4^-$, or $SHI{-}HSO_4^-$), and H_3PO_4 ($SEA{-}H_3PO_4$, $SEC{-}H_2PO_4^-$, or $SHI{-}H_2PO_4^-$) and analyzed with thermogravimetry (TG) under dynamic and isothermal conditions in nitrogen or oxygen environment. According to the values of thermooxidation maxima (TM) calculated from the maximal difference of measured residues on the dynamic TG curves run in nitrogen and oxygen environments the order of decreasing thermooxidation resistance is: $S > SEA{-}H_3PO_4 > SHI{-}H_2PO_4^- > SHI{-}HSO_4^- > SEA{-}H_2SO_4 > SEC{-}HSO_4^- > SEC{-}HO^- > SEA{-}HCl > HCl{-}Cl^- > SEC{-}Cl^- > SHI{-}HO^- > SEA > SEC{-}H_2PO_4^- > SE$. The first-order rate constants calculated by the linear regression method (regression coefficient $R > 0.95$) represented the initial rate constants for residue formation (k_r's) and gasification (k_g's). All the derivatives had greater values of rate constants than S and the k_g's were about 1000 times greater than k_r's. The values obtained in nitrogen were smaller than those calculated from runs in oxygen environment with the exception of S. Most of the salt forms had greater values of k_g's in oxygen environment. The activation energies (E's) were usually greater in nitrogen than in oxygen as well as for residue formation than for gasification. The $SHI{-}HO^-$ sample had high k_g's and low E_g's in oxygen environment while for $SHI{-}H_2SO_4^-$ the opposite was true. This we consider as two extremes for labile and resistant samples for gasification. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Starch; Thermogravimetry; Cross-linking; Ion-exchangers; Thermooxidation; Residue; Gasification

1. Introduction

The cross-linking of starch using 1,3-bis(3-chloro-2-hydroxypropyl)imidazolium hydrogen sulfate or epichlorohydrin (E) in the presence of NH_4OH or choline was studied with the goal to prepare water-insoluble materials with ion-exchanging properties (Šimkovic, Francis, & Reeves, 1997; Šimkovic, Hricovíni, & Sasinková, 2002; Šimkovic, Laszlo, & Thompson, 1996). These materials might find application as disposable traps for environmentally dangerous ions which might be preconcentrated by thermolysis of the polysaccharide component. The presence of oxygen enhances the process. That is why we have studied these derivatives with TG under inert and oxidative environment. The goal was to find out how the material behaves and what could be learnt from calculated rate constants of residue formation/charring and gasification. The samples were analyzed before on Py-GC/MS or TG/MS instruments under inert environment (Šimkovic et al., 1997; Šimkovic & Jakab, 2001). Now we have used different thermobalance and compared the results with data run on TG/MS and additionally studied the thermooxidation which was not possible on Py-GC/MS or TG/MS instruments. The application of the linear regression method for the simultaneous calculation of rate constants of charring and gasification under oxidative conditions was used for the first time. The thermolysis and thermooxidation of quaternary ammonium groups introduced to cellulose and lignocellulosics was also studied by our group (Šimkovic, Antal, Balog, Košík, & Plaček, 1985a; Šimkovic, Antal, Csomorová, & Micko, 1989; Šimkovic, Antal, Mihálov, Königstein, & Micko, 1985b; Šimkovic, & Csomorová, 1998. The oxidative reactions on polysaccharides start below 300 °C and it was assumed that they are independent on the thermal degradation (Shafizadeh & Bradbury, 1979).

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2. Experimental

Partially-hydrolyzed, water-soluble potato starch (S; ZŠ, Dolná Krupá, Slovakia; $M = 19,060$ Da, determined osmometrically); $[\alpha]_D^{20} = +154.0°$ (c 1; H_2O) was used without further treatment. SE derivative was prepared by cross-linking S (1.62 g; 0.01 mol) with E (7.82 ml; 0.1 mol) in water (9 ml; 0.5 mol) and in the presence of NaOH (4 g; 0.1 mol) applying 24 h stirring at room temperature, dialysis, filtration and subsequent freeze drying [115% yield; N = 0%, C = 44.69%, H = 6.87%; DS ($-CH_2CHOHCH_2-$) = 0.01–0.81; DS ($-CH_2CHOHCH_2OH$) = 0.83–2.25]. Under the same conditions, but in the presence of NH_4OH (14.8 ml of 26% solution) SEA derivative {119% yield; N = 3.05%, C = 42.49%, H = 7.38%; DS ($-CH_2CHOHCH_2OH$) = 0.01, DS ($-CH_2CHOHCH_2NH_2$) = 0.01–0.19, DS ($-CH_2CHOHCH_2-NH-CH_2CHOHCH_2OH$) = 0.25–0.53, DS [$-CH_2CHOHCH_2-N(CH_2CHOHCH_2OH)_2$] = 0.19–0.33} was obtained. Part of SEA (0.25 g) was recycled with 5% HCl, H_2SO_4, or H_3PO_4 (100 ml) by stirring for 48 h at room temperature, subsequently washed with excess of deionized water and lyophilized. In this way SEA–HCl {80% yield; Cl = 4.17%, N = 2.19%, C = 41.79%, H = 6.88%; DS [$-CH_2CHOHCH_2-(NH_2^+Cl^-)-CH_2CHOHCH_2OH$] = 0.01–0.05, DS [$-CH_2CHOHCH_2NH_3^+Cl^-$] = 0.01–0.05, DS [$-CH_2CHOHCH_2-(HN^+Cl^-)-(CH_2CHOHCH_2OH)_2$] = 0.41–0.43, DS ($-CH_2CHOH-CH_2OH$) = 0.01}; SEA–$H_2SO_4$ [59% yield; S = 3.66%, N = 2.27%, C = 39.03%, H = 6.75%; DS ($C_6H_{15}O_7NS$) = 0.01–0.09, DS ($C_3H_7O_2$) = 0.01, DS ($C_3H_9O_4NS$) = 0.01–0.07, DS ($C_9H_{21}O_9NS$) = 0.27–0.29]; and SEA–H_3PO_4 [43% yield; P = 2.30%, N = 1.98%, C = 40.03%, H = 6.74%; DS ($C_6H_{15}O_7NP$) = 0.01, DS ($C_3H_7O_2$) = 0.01, DS ($C_3H_9O_4NP$) = 0.01, DS ($C_9H_{21}O_9NP$) = 0.29] samples were obtained.

SEC–HO^- was prepared by mixing S (1.62 g; 0.01 mol) with water (3.6 ml; 0.2 mol) containing NaOH (4 g; 0.1 mol) and after homogenization choline chloride (0.698 g, 5 mmol; Aldrich) was added and subsequently 1.96 ml (0.025 mol) of E and stirred for 24 h at room temperature. After washing with deionzed water through fritted glass (G4) until neutral reaction on pH-paper, subsequently with ethanol and dried to constant weight in vacuo 1.98 g {122% yield; N = 1.25%, C = 43.87%, H = 7.40%; DS ($-CH_2CHOHCH_2-OCH_2CH_2^+N(CH_3)_3^-OH$] = 0.37, DS ($C_3H_7O_2$) = 0.01–1.15, DS ($C_3H_6O$) = 0.01–0.65} of the derivative was obtained. Analogically as above parts of SEC–HO^- (0.25 g) was recycled to SEC–Cl^- [81%; N = 1.26%, C = 43.45%, H = 7.59%, Cl = 2.71%; DS ($C_8H_{19}O_2NCl$) = 0.17–0.33, DS ($C_3H_7O_2$) = 0.01–0.07, DS (C_3H_6O) = 0.01–1.05], SEC–HSO_4^- (83%, N = 1.27%, C = 42.31%, H = 7.56%, S = 2.16%; DS ($C_8H_{19}O_6NS$) = 0.11–0.16, DS ($C_3H_7O_2$) = 0.01–2.13, DS (C_3H_6O) = 0.01–1.21] and SEC–$H_2PO_4^-$ [86%, N = 1.15%, C = 41.39%, H = 7.06%, P = 1.79%; DS ($C_8H_{19}O_6NP$) = 0.23–0.25, DS ($C_3H_7O_2$) = 0.01–1.43, DS (C_3H_6O) = 0.01–1,41] form.

SHI–HO^- was prepared by dissolving S (1.62 g, 0.01 mol) in water (6 ml, 0.333 mol) containing NaOH (0.952 g, 0.024 mol) and subsequent adding of BCHIHS (3.76 g, 0.01 mol) and stirring for 24 h at room temperature. Analogically as above the sample in 159% yield was obtained (N = 5.18%,C = 43.39%,H = 6.93%) and parts (0.25 g) were recycled to SHI–Cl^- form (58% yield, N = 4.61%, C = 40.37%, H = 6.18%, Cl = 3.57%; DS ($-CH_2CHOH-CH_2(N_2C_3H_3)(^-OH)CH_2CHOHCH_2-$) = 0.01–0.73, DS ($-CH_2-CHOH-CH_2-(N_2C_3H_3)(^-OH)CH_2CHOHCH_2OH$) = 0.01–0.79], SHI–$H_2SO_4^-$ salt [71%, N = 4.77%, C = 41.39%, H = 6.35%, S = 2.99%; DS ($C_9H_{15}O_6N_2S$) = 0.07–0.25, DS ($C_9H_{16}O_7N_2S$) = 0.01–0.15] or SHI–$H_2PO_4^-$ sample (65%, N = 4.60%, C = 38.24%, H = 3.11%, P = 2.33%; DS ($C_9H_{16}O_7N_2P$) = 0.25–0.41, DS ($C_9H_{16}O_7N_2P$) = 0.01–0.15].

Thermogravimetry (TG) was run on Perkin–Elmer TGS-1 instrument in a static nitrogen or oxygen atmosphere using a heating rate 10 K/min for dynamic conditions. The sample weights were in 1 mg scale (Al pan), and the temperature values were calculated using ferromagnetic standards. In the case of isothermal measurements the temperature used was attained at a rate of 160 K/min. The rate constants of residue formation or charring (k_r) were calculated from the time dependency $\ln(m_0/m_t) = f(t)$ using a linear regression method, where m_0 is the weight of the sample at the moment of reaching the desired temperature and m_t is the weight of the sample after time t of isothermal heating. The rate constants of gasification (k_g) were calculated from the $\ln(1/m_0 - m_t) = f(t)$ function. Only values which were measured during the first 2 min of thermolysis were used. The rate constants fitted first-order rates (which was statistically evaluated by the regression coefficient $R > 0.95$) and were considered as the starting rates of residue formation or gasification.

The elemental analysis were run on a Fision EA-1108 instrument and the DS values were calculated as described earlier (Horton & Pardoe, 1970).

3. Results and discussion

The prepared samples could be divided into weakly basic amine derivatives cross-linked with E (SEA, SEA–HCl, SEA–H_2SO_4 and SEA–H_3PO_4) and strongly basic quaternary starches. First type of quaternized derivatives contains choline group cross-linked with E, which could be transfered to Cl^- (SEC–Cl^-), $H_2PO_4^-$ (SEC–$H_2PO_4^-$), HSO_4^- (SEC–HSO_4^-) or HO^- form (SEC–HO^-), while the second type derivative contains dihydroxypropylimidazolium group (SHI–Cl^-, SHI–$H_2PO_4^-$, SHI–HSO_4^- or SHI–HO^-). In all cases part of the cross-linking agent is linked only monofunctionally as calculated from elemental analysis (see Section 2). The molar ratios of N to S or P or Cl were in the range of expected structural relations of the ion-exchanging groups and calculated DS values. For the

Table 1
Results of dynamic TG measurements of S and its derivatives in inert and oxidative environments (the residues of samples in wt%)

Sample	Environment	Temperature (°C)											
		105	250	275	300	325	350	375	400	425	450	475	500
S	Nitrogen	97	95	93	84	65	58	55	53	50	49	47	46
	Oxygen	98	95	94	89	73	59	53	49	43	36	28	21
SE	Nitrogen	98	98	98	98	92	69	43	28	22	21	21	20
	Oxygen	94	94	92	74	47	34	29	25	23	19	13	8
SEA	Nitrogen	98	97	94	78	57	45	39	36	34	32	31	30
	Oxygen	95	85	73	60	47	41	37	33	29	24	18	13
SEA–HCl	Nitrogen	97	90	70	63	58	54	51	49	48	46	44	43
	Oxygen	96	75	64	54	45	40	35	31	26	19	13	10
SEA–H_2SO_4	Nitrogen	97	87	74	68	62	56	52	49	47	45	44	43
	Oxygen	96	83	69	60	50	44	39	34	28	22	15	12
SEA–H_3PO_4	Nitrogen	97	93	75	65	61	57	55	54	53	51	50	47
	Oxygen	97	91	71	63	58	55	52	49	44	39	32	28
SEC–H_3PO_4	Nitrogen	96	94	89	59	51	46	44	43	43	41	40	38
	Oxygen	98	91	62	53	48	46	44	41	38	34	29	23
SEC–Cl^-	Nitrogen	97	91	87	72	53	40	32	26	24	23	22	22
	Oxygen	96	89	75	54	41	35	31	28	25	20	15	13
SEC–HSO_4^-	Nitrogen	97	96	90	72	51	43	38	34	31	30	28	27
	Oxygen	97	93	79	57	46	39	36	32	29	23	17	11
SEC–HO^-	Nitrogen	96	86	81	69	46	39	33	28	26	25	24	22
	Oxygen	98	81	69	54	44	39	36	33	29	24	18	17
SHI–Cl^-	Nitrogen	96	92	84	67	46	37	35	33	32	32	31	30
	Oxygen	97	90	68	54	45	39	34	30	26	21	16	13
SHI–HO^-	Nitrogen	96	84	78	64	44	37	34	33	32	31	30	29
	Oxygen	94	72	58	48	40	34	30	27	22	17	11	10
SHI–$H_2PO_4^-$	Nitrogen	97	96	94	77	65	60	59	57	56	54	53	52
	Oxygen	96	93	86	72	62	58	55	52	48	43	37	34
SHI–HSO_4^-	Nitrogen	95	94	84	68	56	47	42	41	39	38	37	36
	Oxygen	97	93	76	64	57	43	36	32	28	23	17	1

quaternary derivatives the DS values are greater than for amine samples. As seen from DS values of the same type of ion-exchanging group, the recycling to different cycles gave slightly different DSs for these cycles, which might be related with accessibility of the groups. The results of dynamic TG measurements are listed in Table 1.

Under nitrogen environment the most intense degradation take place around 325 °C where the thermal stability decreases in order: SE > S = SHI–$H_2PO_4^-$ > SEA–H_2SO_4 > SEA–H_3PO_4 > SEA–HCl > SEA > SHI–HSO_4^- > SEC–Cl^- > SEC–$H_2PO_4^-$ = SEC–HSO_4^- > SEC–HO^- = SHI–Cl^- > SHI–HO^-. Under oxygen atmosphere at 300 °C the thermooxidation stability decreases: S > SE > SHI–$H_2PO_4^-$ > SHI–HSO_4^- > SEA–H_3PO_4 > SEA = SEA–H_2SO_4 > SEC–HSO_4^- > SEC–Cl^- = SHI–Cl^- = SEA–HCl = SEC–HO^- > SEC–$H_2PO_4^-$ > SHI–HO^-. In both lists the SHI–HO^- sample was the most degraded one and also SEC–HO^- was close to the end of both lists. On the other hand the most stable were S and SE samples.

For all the modified samples the residue formed in oxygen at certain temperature is smaller than in nitrogen. Only S has greater residue in oxygen up to 350 °C. This phenomenon, thermooxidation was observed on different polysaccharides and lignocellulosics (Šimkovic et al., 1985a; Šimkovic et al., 1989; Šimkovic, Balog, & Csomorová, 1995; Šimkovic, & Csomorová, 1998; Šimkovic, Pastýr, Csomorová, Balog, & Micko, 1990). When we follow this difference with increasing temperature, than at certain temperature it reaches a maximum, that we could call thermooxidation maximum (TM). So in this way we could make an order of decreasing thermooxidation resistance according to the decreasing TM values at listed temperatures: S (8%/325 °C) > SEA–H_3PO_4 (−3/325) > SHI–$H_2PO_4^-$ (−8/275) > SHI–HSO_4^- (−8/275) > SEA–H_2SO_4 (−12/325) > SEC–HSO_4^- (−15/300) > SEC–HO^- (−15/300) > SEA–HCl (−15/250) > SHI–Cl^- (−16/275) > SEC–Cl^- (−18/300) > SHI–HO^- (−20/275) > SEA (−21/275) > SEC–$H_2PO_4^-$ (−27/275) > SE (−45/325). As seen after S the SEA–H_3PO_4 sample is the most resistant followed by SHI–H_3PO_4 with the same TM as SHI–H_2SO_4 but with 10% greater residues (Table 1). The most degraded sample with TM at 275 °C is SEC–$H_2PO_4^-$, but also SEA–HCl is considered as labile due to TM at lowest temperature (250 °C).

The first-order initial rate constants of residue formation/charring (k_r's) and gasification (k_g's) in nitrogen and oxygen calculated by the linear regression method are listed in Table 2. The k_r's are smaller than k_g's in both environments. In oxygen the corresponding k's are smaller than in nitrogen only for S. For all the other samples the opposite is true. The

Table 2
Isothermal TG data of S and its derivatives (the values of k_r and k_g are multiplied by 1000)

Sample	Environment		Rate constants (min^{-1})					Activation energies (kJ/mol)
			250 (°C)	260 (°C)	270 (°C)	280 (°C)	290 (°C)	
S	Nitrogen	k_r	3	9	15	39	70	195
		k_g	420	682	1214	1511	2017	97
	Oxygen	k_r	1	2	18	35	36	230
		k_g	382	420	584	881	914	69
SE	Nitrogen	k_r	1	1	12	3	11	168
		k_g	6	23	76	246	761	293
	Oxygen	k_r	3	7	8	23	28	134
		k_g	421	548	687	945	1162	63
SEA	Nitrogen	k_r	15	42	43	103	167	140
		k_g	324	714	746	2283	3277	142
	Oxygen	k_r	58	118	162	271	396	115
		k_g	1251	1471	1822	2156	3312	51
SEA–HCl	Nitrogen	k_r	132	270	625	782	1615	145
		k_g	1338	2384	5604	6203	8076	112
	Oxygen	k_r	161	397	892	1431	2416	164
		k_g	4806	13238	21354	47067	93051	176
SEA–H_2SO_4	Nitrogen	k_r	85	158	308	483	613	125
		k_g	1385	1977	3644	3859	3953	68
	Oxygen	k_r	179	233	266	564	734	90
		k_g	6186	8019	10633	12813	16438	59
SEA–H_3PO_4	Nitrogen	k_r	20	51	149	351	797	228
		k_g	344	815	2013	4603	9642	206
	Oxygen	k_r	39	96	180	366	572	164
		k_g	2829	4123	8400	13943	16186	115
SEC–$H_2PO_4^-$	Nitrogen	k_r	6	12	49	77	202	223
		k_g	211	557	941	2070	4180	178
	Oxygen	k_r	43	108	268	353	723	167
		k_g	1620	2749	6684	10173	12918	134
SEC–Cl^-	Nitrogen	k_r	22	66	71	84	104	78
		k_g	641	1151	1164	1544	2027	70
	Oxygen	k_r	120	175	177	358	749	107
		k_g	4492	5867	7630	9587	12794	63
SEC–HSO_4^-	Nitrogen	k_r	8	19	41	90	187	193
		k_g	296	719	1436	1515	3486	139
	Oxygen	k_r	39	87	146	324	513	159
		k_g	1785	2440	4652	8968	12371	127
SEC–HO^-	Nitrogen	k_r	20	34	36	52	98	88
		k_g	288	468	766	1108	1856	112
	Oxygen	k_r	164	193	254	489	646	90
		k_g	3031	3691	4541	5205	6004	50
SHI–Cl^-	Nitrogen	k_r	24	35	65	149	262	327
		k_g	706	911	919	2211	3717	102
	Oxygen	k_r	85	169	265	487	494	113
		k_g	3830	7024	8573	15003	21601	103
SHI–HO^-	Nitrogen	k_r	7	15	35	146	158	212
		k_g	391	643	959	1541	2385	110
	Oxygen	k_r	386	476	555	963	907	69
		k_g	13527	16553	14721	27293	33697	57
SHI–$H_2PO_4^-$	Nitrogen	k_r	5	11	25	54	113	192
		k_g	138	355	946	1841	5317	219
	Oxygen	k_r	17	24	52	103	154	143
		k_g	461	860	1930	3705	5923	161
SHI–HSO_4^-	Nitrogen	k_r	17	33	69	123	205	155
		k_g	682	1460	2985	6296	12328	178
	Oxygen	k_r	43	94	159	243	482	142
		k_g	2366	4194	6904	12232	19895	130

activation energy for residue formation on S is greater in oxidative than in inert environment, but the value for gasification is smaller and the one obtained in oxygen is smaller than the value measured in nitrogen. This confirms that more energy is needed for processes which are taking place in residue than for the gasification and also the thermooxidation is less energy consuming than thermolysis. When we put the samples into order according to the increasing k_r's in nitrogen (SE > S > SHI–$H_2PO_4^-$ > SHI–HO^- > SEC–HO^- > SEC − HSO_4^- > SEA > SEC –$H_2PO_4^-$ > SHI–Cl^- > SHI–HSO_4^- > SEC–Cl^- > SEA–H_3PO_4 > SEA–H_2SO_4 > SO–HCl), than we can assume that in the inert environment the quaternized derivatives are more stable than weak amine samples in acid forms. The corresponding activation energies are decreasing in order: SHI–Cl^- > SEA − H_3PO_4 > SEC–$H_2PO_4^-$ > SHI–HO^- > S > SEC–H_2SO_4 > SHI–$H_2PO_4^-$ > SE > SHI–; HSO_4^- > SEA–HCl > SEA > SEA–H_2SO_4 > SEC–HO^- > SEC–Cl^-. It seems that in nitrogen the $H_2PO_4^-$/H_3PO_4 samples are more stable than Cl^-/HCl forms. According to increasing k_g's (SE > SEA > SEC–HO^- > SHI–Cl^- > SEC–$H_2PO_4^-$ > SHI–$H_2PO_4^-$ > SHI–HO^- > SEC–Cl^- > S > SEC–HSO_4^- > SEA–H_3PO_4 > SHI–HSO_4^- > SEA–H_2SO_4 > SEA–HCl) the SEA–HCl sample is forming residue with the greatest speed while the related activation energies are decreasing in order: SE > SHI–$H_2PO_4^-$ > SEA–H_3PO_4 > SHI–HSO_4^- = SEC–$H_2PO_4^-$ > SEA > SEC–HSO_4^- > SEA–HCl = SEC–HO^- > SHI–HO^- > SHI–Cl^- > S > SEC–Cl^- > SEA–H_2SO_4. These results indicate that HCl/Cl^- samples are gasified in nitrogen easier than others as seen from their high *k*'s and low *E*'s. In oxygen the k_r's are increasing as follows: SE > S > SHI–$H_2PO_4^-$ > SEC–HSO_4^- > SHI–HSO_4^- > SEA > SEC–Cl^- > SEA–H_3PO_4 > SEC–HO^- > SHI–Cl^- > SEA–H_2SO_4 > SEC–$H_2PO_4^-$ > SHI–HO^- > SEA–HCl and E_r's are decreasing: S > SEC–$H_2PO_4^-$ > SEA–HCl = SEA–$H_2PO_4^-$ > SEC–HSO_4^- > SHI–$H_2PO_4^-$ > SHI–HSO_4–SE > SEA > SHI–Cl^- > SEC–Cl^- > SEA–H_2SO_4 = SEC–HO^- > SHI–HO^-. It shows again that after SE and S the SHI–$H_2PO_4^-$ has the smallest k_r's, while according to E_r's only S is more stable than SEC–$H_2PO_4^-$. The SHI–HO^- sample is among those which are easy-forming the residue. The k_g's are under analogical conditions increasing (S > SE > SEA > SHI–$H_2PO_4^-$ > SEC–HO^- > SEC–HSO_4^- > SEC–$H_2PO_4^-$ > SHI–HSO_4^- > SEC–Cl^- > SEA–H_3PO_4 > SHI–Cl^- > SEA–H_2SO_4 > SHI–HO^- > SEA–HCl) and E_g's decreasing (SEA–HCl > SHI–$H_2PO_4^-$ > SEC–$H_2PO_4^-$ > SHI–HSO_4^- > SEC–HSO_4^- > SEA–H_3PO_4 > SHI–Cl^- > S > SE = SEC–Cl^- > SEA–H_2SO_4 > SHI–HO^- > SEA > SEC–HO^-) showing that SHI–HO^- sample has high k_g's and low E_g. The SHI–$H_2PO_4^-$ sample proved to be again one of the most resistant. The SEA–HCl has the greatest *k* values and also the greatest E_g, which indicates different mechanism of gasification in presence of acid than on quaternary samples where only ion catalysis the dehydration.

The values of k_r's and k_g's of S, SE, SEA, SEA–HCl, SEA–H_2SO_4 and SEA–H_3PO_4 measured before on different thermobalance are exhibiting the same trend although giving slightly different absolute values as could be expected due to different conditions used on TG and TG/MS instruments (Šimkovic, & Jakab, 2001). It seams that the SEA–H_3PO_4, SEC–$H_2PO_4^-$ and SHI–$H_2PO_4^-$ samples are the most resistant towards thermooxidation/gasification. It is hard to predict any reaction schemes before developing a suitable technique for analyzing the gases in the presence of oxygen or to develop a method for measuring of oxygen consumption under the used conditions.

4. Conclusions

According to the dynamic TG measurements of amine and ammonium derivatives in nitrogen and oxygen environment it could be concluded that the thermooxidation resistance is decreasing in order: S > SEA–H_3PO_4 > SHI–$H_2PO_4^-$ > SHI–HSO_4^- > SEA–H_2SO_4 > SEC–HSO_4^- > SEC–HO^- > SEA–HCl > SHI–Cl^- > SEC–Cl^- > SHI–HO^- > SEA > SEC–$H_2PO_4^-$ > SE. The isothermal experiments indicate that the SEA–H_3PO_4, SEC–$H_2PO_4^-$ and SHI–$H_2PO_4^-$ are the most resistant towards both thermolysis and thermooxidation. For gasification in presence of oxygen the SHI–HO^- seems to be the most easily gasified sample (with the biggest k_g's and smallest E_g.

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