

CHEMICAL TRANSFORMATIONS OF POLYMERS. VIII.*

DEGRADATION OF CROSSLINKED
POLY[(VINYL BENZYL)TRIMETHYLAMMONIUM HYDROXIDE]
AND ITS LOW MOLECULAR WEIGHT MODELS
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Received March 9th, 1970

Crosslinked poly[(vinyl benzyl)trimethylammonium hydroxide], a styrene type anion exchanger decomposes under the influence of hydroxyl ions at elevated temperature to the products containing mainly benzyl alcohol and benzyldimethylamino groups. The reaction is faster at presence of oxygen which partially oxidizes alcohols to carboxylic acids. Judging from the behaviour of model compounds, the oxidation of polyvinyl chain is likely to occur at the advanced stage of degradation of an anion exchanger but only to a very small extent.

Styrene-type anion exchangers based on crosslinked poly[(vinyl benzyl)trimethylammonium hydroxide], when used for long periods of time, progressively lose their ability to exchange ions. One of the reasons for this is their chemical degradation by hydroxyl ions¹ or by oxygen dissolved in water²; the process may be accelerated by elevated temperature, catalytic activity of metals^{2,3} or by radioactive exposure⁴.

Over the period of five years we have been following the behaviour of styrene anion exchangers used under plant conditions in filters as well as the changes of the anion exchanger in testing baskets^{5,6}. Simultaneously, experiments on model compounds have been performed. This paper supplements the previous work¹ in which a comparison was made of stabilities of poly [(vinyl benzyl)-trimethylammonium hydroxide] with other polymer and low molecular weight quaternary ammonium bases. The products of degradation of styrene anion exchanger and its low molecular weight models in a nitrogen or oxygen atmosphere have been identified. The results enhance the knowledge as to the structural changes in an anion exchanger during the degradative process.

* Part VII: This Journal 33, 3281 (1968).

EXPERIMENTAL

Compounds for Degradation

Anion exchanger S-8-TM is a commercial product of VÚSPL, Pardubice, based on crosslinked (8% divinylbenzene) poly[(vinyl benzyl)trimethylammonium hydroxide]; its overall exchange capacity is 3.55 meq/g. (Isopropylbenzyl)-trimethylammonium chloride (for $C_{13}H_{22}ClN$ (227.8), calculated: 68.55% C, 9.74% H, 6.15% N, 15.56% Cl; found: 68.06% C, 9.98% H, 6.02% N, 16.04% Cl) and benzyltrimethylammonium chloride (for $C_{10}H_{16}ClN$ (185.7), calculated: 64.68% C, 8.68% H, 19.09% Cl, 7.54% N; found: 64.62% C, 8.75% H, 18.56% Cl, 7.57% N) were prepared⁷ by reaction of trimethylamine with isopropylbenzyl chloride⁸ (b.p. 125–129°C/40 Torr) and benzyl chloride, respectively.

Degradation

Reactions in 10M-KOH at 110°C were performed using previously described apparatus¹; in addition to it, two cooled traps (–78°C) were connected to the absorption flask to collect neutral volatile products. The flowrate of nitrogen and oxygen, respectively, was always 3 ml/s. The alkaline liquid from the reactor was extracted with ether and the extract separated into two layers, by extraction with dilute hydrochloric acid. The ether layer contained alcohols and aldehydes whereas the water layer dissolved amines. Carboxylic acids were then isolated by ether extraction of acidified reaction liquid. The quarternary ammonium bases that did not degrade remained in the water layer. Volatile amines were absorbed in the absorption flask and neutral volatile products condensed in the cooled traps.

Analytical Methods

Whatman No 3 paper was used for descending *paper chromatography*. Alcohols (in form of their 3,5-dinitrobenzoates) and aldehydes (in form of their 2,4-dinitrophenylhydrazones) were separated on the paper impregnated by 25% solution of dimethylformamide in ethanol, cyclohexane being the mobile phase. Alcohols were first reduced by stannous chloride in hydrochloric acid and then detected by 1% solution of *p*-dimethylaminobenzaldehyde in ethanolic hydrochloric acid. The 2,4-dinitrophenylhydrazones of carbonyl compounds were detected by reaction with 1% ethanolic solution of NaOH⁹. Amines were separated in the system containing 5% KCl in water-butanol solution which was previously shaken with saturated solution of potassium chloride in water. Quarternary ammonium bases were, besides this method, in the system laurylalcohol-ethanol mixed with 1M-HCl (1 : 1). Primary amines were detected by 0.2% ethanolic solution of ninhydrine, secondary amines by 5% solution of sodium nitroprusside in 10% acetaldehyde in water to which 2% of Na_2CO_3 was added. Tertiary amines and quarternary bases were developed by the Dragendorff solution or by potassium iodoplatinate solution⁹.

Gas chromatography was performed using a Panchromatograph (PYE) instrument fitted with a flame ionization detector (Detector voltage 50 V). Two kinds of column packings were used in a 1.5 m long column: A-Chromosorb W (treated with hydrochloric acid) with Apiezon L (20% w/w) as a stationary phase. B-Chromosorb W with 20% w/w of poly(ethylene glycoladipate). Both column packings (particle size 0.10–0.16 mm) were preheated for 24 hours at 210°C under a stream of nitrogen. The sampling into the column was effected by a Hamilton microsyringe. Mixtures of alcohols with aldehydes and water solutions of amines, respectively, were separated at 160°C; the flow rate of nitrogen: 57 ml/min (packing A) and 68 ml/min (packing B); hydrogen

flow rates: 41 ml/min (A) and 34 ml/min (B). The acids in form of their methylesters^{10,11} were separated at 201°C, the flow rate of nitrogen being 62 ml/min (A) and 77 ml/min (B), respectively. The hydrogen flowrate was 45 ml/min (A) and 41 ml/min (B), respectively. Retention times of the degradation products and those of authentic specimens were expressed by indexes due Kovats¹²⁻¹⁴.

Other analytical methods. Trimethylamine and methanol were identified in form of a picrate and 3,5-dinitrobenzoate, respectively. The mixture of acids isolated from the main product of degradation of isopropylbenzyl trimethylammonium hydroxide under oxygen was separated using a preparative gas chromatograph Fractometer 116 E Perkin-Elmer. The main component was identified by NMR spectrometry (JNM-3-60) as methylester of *p*-isopropylbenzoic acid. N,N-dimethylbenzamid and N,N-dimethylisopropylbenzamid were determined in the degradation products, by melting the compound with fluorescein chloride¹⁵. Peroxides were determined polarographically using an LP-55 instrument combined with an EZ-2 register (Laboratory equipment, Prague); 0.2M LiCl-dissolved in the mixture of methanol-benzene (1 : 2)¹⁶ was used as an electrolyte. The carbonyl groups of the degraded anion exchanger were determined with the help of the Girard reagent by comparison of nitrogen content before and after the reaction.

RESULTS AND DISCUSSION

Anion exchanger S-8-TM at increased temperature loses trimethylamine, the amount of which is proportional to the hydroxyl ions concentration; the dependence of molar conversion of degradation is shown in Fig. 1. A comparison with our previous results

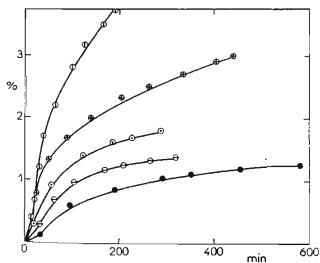


FIG. 1

Degradation of an S-8-TM Anion Exchanger in an Inert Atmosphere (1 ml N_2/s) at 95°C

Environment (sample size): ● demineralized water (2.67 mval), ○ 1M-NaOH (4.13 mval), ⊙ 3M-NaOH (2.11 mval), ⊕ 5M-NaOH (2.51 mval), ⊕ 10M-NaOH (2.50 mval).

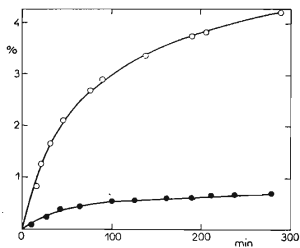


FIG. 2

Comparison of an Anion-Exchange Resin Prepared in the Laboratory (L)¹ with a Commercial Anion Exchanger S-8-TM in Water

○ (4.08 mval/g)¹, ● S-8-TM (3.55 mval/g).

have shown, that the rate of degradation increases with increasing capacity of an exchanger (Fig. 2); this is due to higher concentration of quarternary ammonium groups and corresponding hydroxyl ions and also due to greater swelling capacity of an anion exchanger thus enhancing the diffusion in the gel phase. The presence of oxygen accelerates trimethylamine evolution both in deionized water (Fig. 3) and in 10M-NaOH solutions.

Methanol was isolated as another product of anion exchanger degradation besides trimethylamine. Traces of methylamine and dimethylamine in the degradation products were determined by means of paper chromatography. The presence of corresponding benzylalcohol and benzyldimethylamine groups formed in an anion exchanger in the process of degradation causes decrease in total exchanger capacity and an increase in weak-base capacity.

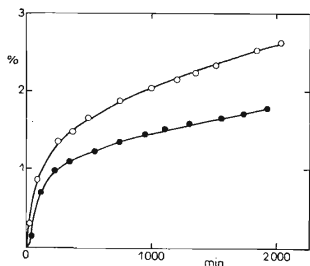
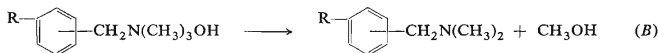
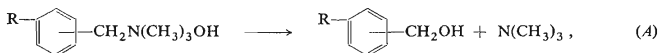


FIG. 3

Degradation of an S-8-TM Anion Exchanger in Demineralized Water at 95°C (flow rate of gas 1 ml/s)

Atmosphere (sample size): ● nitrogen (2.67 mval), ○ oxygen (2.96 mval).

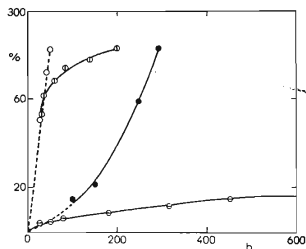


FIG. 4

Comparison of an S-8-TM Anion Exchanger Degradation with (Isopropylbenzyl)trimethylammonium Hydroxide (I) Degradation in an Oxidative Atmosphere, (oxygen flow rate 3 ml/s) at 110°C

○ Anion exchanger 19.97 mval, demineralized water; ○ anion exchanger 4.26 mval, 10M-KOH; ● I 2.67 mval, demineralized water; ○ I 1.92 mval, 10M-KOH.

TABLE I

Degradation of an S-8-TM Anion Exchanger
Capacities (mval/g): C_t total, C_b weak-base.

Time h	Inert atmosphere		Oxidative atmosphere	
	C_t	C_b	C_t	C_b
0	3.55	0.00	3.55	0.00
26	2.60	0.73	2.17	1.11
38	2.26	1.02	1.78	1.35
60.5	2.32	1.73	1.56	1.45
83.5	1.41	1.32	1.46	1.40
140	1.36	1.31	1.47	1.40
200	1.40	1.35	1.58	1.54

The results in Table I indicate that the proportion of reactions *A* and *B* is in the ratio 3 : 2. The data obtained from the experiments under power-plant conditions⁶ indicated a 10–20% higher extent of reaction *A* than under laboratory conditions. This difference can be accounted for a decrease of total capacity under plant conditions, caused by contamination by organic substances. By measuring weak acidic capacity of samples (method used for amphoteric exchangers¹⁷) it was possible to determine the carboxyl groups contents in the final stage of degradation. The samples degraded in the presence of oxygen contained almost one percent of the carboxyl groups whereas those degraded in an inert atmosphere contained half of this value. (Compare with ref.^{3,18}). The attempts to show the presence of aldehydic groups – transition oxidative intermediates were, however, unsuccessful.

Model compounds were used for more detail degradation studies. An oligomeric model of an anion exchanger was not considered necessary because of a small probability of mutual interaction of structural units. (Isopropylbenzyl)trimethylammonium-hydroxide (*I*)* was used as a structural unit model knowing, that its isopropyl group is more reactive than the polyvinyl chain of an anion exchanger whose tertiary carbon is less accessible¹⁹. Isopropylbenzylalcohol as well as (isopropylbenzyl)dimethylamine were used as degradation products models* whereas benzyltrimethylammonium-hydroxide (*II*) model was used to distinguish between reactions on the trimethylammonium group and those taking place on the isopropyl group.

* The stereoisomers of 7-chlorocymene obtained by chloromethylation of cumene (first preparation step) were not separated from one another in order to obtain a better model of polystyrene chlormethylation.

The structural unit model gave up trimethylamine whose rate of evolution was, at the early stage of reaction, identical with that measured for an anion exchanger but the rate increased with the conversion (Fig. 4). The deceleration of anion exchanger degradation has been explained by slower diffusion caused by the decrease in the concentration of hydrophilic groups¹.

The compounds formed by degradation of models *I* and *II* are listed in Table II. Only reactions *A* and *B* take place in an inert medium. Besides these reactions there is oxidation of original trimethylammoniomethyl and isopropyl groups which takes place at presence of oxygen. The primary step is probably the attack on nitrogen substituent, judging from the fact that only a quaternary ammonium compound of the original structure was found amongst the degradation products of model *I*. An independent experiment confirmed that the (isopropylbenzyl)dimethylamine did not undergo further changes at given experimental conditions. The presence of formaldehyde is connected not only with the oxidation of methanol but also with the oxidation of trimethylamine because traces of dimethylamine and methylamine were found to be present in the system. Thus the most important oxidative changes in an anion exchanger being degraded are the benzylalcohol group oxidation and isopropylbenzylalcohol group oxidation, respectively. There were no peroxides found among the reaction products. This indicates their fast alkaline-induced splitting. Benzene-

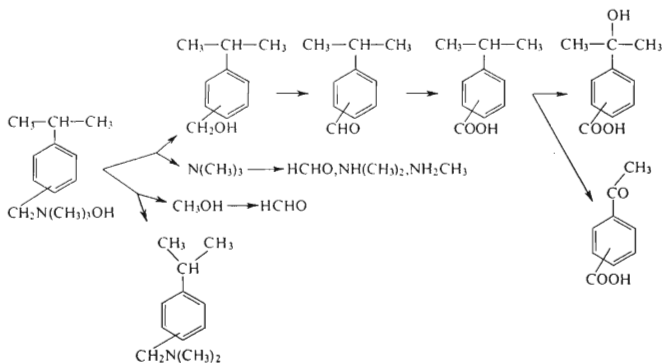
TABLE II

Compounds Found After Degradation of (Isopropylbenzyl)Trimethylammonium Hydroxide (*I*) and Benzyltrimethylammonium Hydroxide (*II*) in an Oxygen Atmosphere

Compound	<i>I</i>	<i>II</i>	Method ^a	Compound	<i>I</i>	<i>II</i>	Method ^a
$(\text{CH}_3)_2\text{CH}-\phi-\text{CH}_2\text{N}(\text{CH}_3)_3$ OH	+		PC	$\phi-\text{CH}_2\text{OH}$		+ ^b	GC
$\phi-\text{CH}_2\text{N}(\text{CH}_3)_3\text{OH}$		+ ^b	PC	CH_3OH	+ + ^b		M
$(\text{CH}_3)_2\text{CH}-\phi-\text{CH}_2\text{N}(\text{CH}_3)_2$	+		PC, GC	$(\text{CH}_3)_2\text{CH}-\phi-\text{CHO}$	+		PC, GC
$\phi-\text{CH}_2\text{N}(\text{CH}_3)_2$		+ ^b	PC	$\phi-\text{CHO}$		+	PC, GC
$\text{N}(\text{CH}_3)_3$	+	+ ^b	PC, M	HCHO	+	+	PC
$\text{NH}(\text{CH}_3)_2$		+ ^c	PC	$(\text{CH}_3)_2\text{CH}-\phi-\text{COOH}$	+		GC, NMR
NH_2CH_3	+ ^c	+ ^c	PC	$(\text{CH}_3)_2(\text{OH})\text{C}-\phi-$ -COOH	+		GC
$(\text{CH}_3)_2\text{CH}-\phi-\text{CH}_2\text{OH}$	+		PC, GC	$\text{CH}_3\text{CO}-\phi-\text{COOH}$	+		GC
				$\phi-\text{COOH}$	+		GC

^a PC paper chromatography, GC gas chromatography, M melting point of a compound mixed with an authentic specimen. ^b Found also in an inert atmosphere degradation. ^c Traces.

dicarboxylic acids and *N,N*-dimethylisopropylbenzamid were not found either. The existence of small quantities of resinous products can be accounted for by occurrence of aldehydes and/or transition derivatives of methylstyrene in the reaction mixture. Finally, the oxidative degradation of model *I* can be described by the following scheme



With regard to the low reactivity of sterically hindered tertiary carbon atoms of the polyvinyl substituent it is likely that in polymeric system the oxidation of the original exchange group will predominate.

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Translated by J. Sedlář.