

Reactions of Trithiocyanuric Acid with Oxiranes. III. Reactions with Epichlorohydrin

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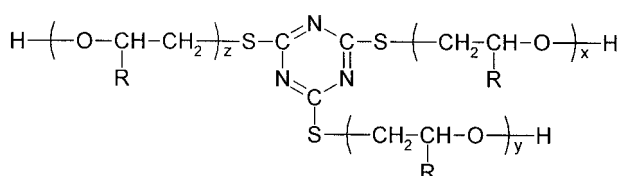
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ABSTRACT: Reactions of trithiocyanuric acid with an excess of epichlorohydrin were investigated. Trifunctional polyetherols containing the *s*-triazine ring were prepared. The structure of the products was verified using elemental analysis, ¹H-NMR, and IR techniques. Some of the physical properties and the thermal stability of polyetherols were analyzed. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 1154–1160, 2002

Key words: trithiocyanuric acid; epichlorohydrin; reaction course; polyetherols

INTRODUCTION

As previously described,^{1,2} reactions of trithiocyanuric acid (TTCA) with an excess of ethylene oxide or propylene oxide in DMF and in the presence of triethylamine as a catalyst yield polyetherols containing *s*-triazine rings. Their structure can be described by



with R = —H, —CH₃, and

$$6 \leq x + y + z \leq 12$$

The compounds, which have good thermal resistance, can be applied as components of polyurethane foams with improved thermal stability.¹ The kinetics and mechanism of the addition of

TTCA to ethylene oxide and propylene oxide were also described.² This article deals with the addition of the same TTCA to epichlorohydrin (ECH), which is, in practice, an oxirane of a great importance. As an asymmetric compound (like propylene oxide), ECH produces two isometric products: the normal and the abnormal one^{3,4} of the respective moieties:



In reactions with carboxylic acids, the selectivity of ring opening in ECH depends on the acid strength^{5–7} and the kind of catalyst.^{6,8,9} In non-catalyzed reactions, the more of abnormal product formed, the stronger is the acid.⁷

Numerous side reactions accompany the opening of the ECH oxirane ring by an acid, AH.⁵ These are dehydrochlorination of hydroxyesters followed by acid addition to the resulting glycidyl ester, hydrolysis of ECH by residual moisture, etc. The extent of the side reactions depends on the conditions, quality of reagents, kind of catalyst, etc.

Investigations into reactions of ECH with isocyanuric acid revealed that, to obtain chlorohy-

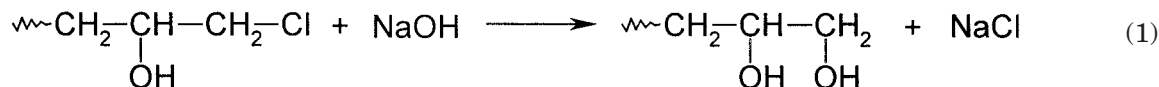
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droxyalkyl derivatives with good yield, a large excess of ECH should be used.¹⁰⁻¹³ The best results are obtained when basic catalysts are used, such as tertiary amines, ammonium bases or their salts, or corresponding ion-exchange resins.^{11,12} With a large excess of ECH and in the presence of a large amount of a basic catalyst

(about 15 wt % with respect to the acid), one obtains triglycidyl isocyanurate, since acid addition is followed by dehydrochlorination.¹⁴

An aqueous NaOH solution is not a suitable catalyst for ECH reactions because it promotes the hydrolysis of the 3-chloro-2-hydroxypropyl group in the product to the 2,3-dihydroxypropyl group¹⁵:



This article reports on attempts to follow the course of the reaction of TTCA with ECH and to determine its similarities and differences to the reaction with ethylene oxide or propylene oxide.

EXPERIMENTAL

Reactions of TTCA with ECH

To a round-bottomed flask (250 cm³) equipped with a reflux condenser, stirrer, and thermometer, 17.7 g (0.1 mol) of TTCA (pure, Aldrich, Steinheim, Germany) and 55.5 g (0.6 mol), 83.3 g (0.9 mol) or 111 g (1.2 mol) of ECH (p.a.; H&W Ltd., Castleford, England) were introduced. The contents were heated to 100°C with continuous stirring. The reactions were conducted at 100°C until the entire amount of ECH had reacted. When 0.6 mol of ECH was used, TTCA dissolved after 25 min (starting from the moment when the temperature of the reaction mixture reached 100°C). The dissolution was accompanied by a high exothermic effect. At different amounts of ECH (0.9, 1.2 mol), the acid dissolved after 50 min with a lower exothermic effect. The end of the reaction was established by determining the epoxy number of the reaction mixture.

Analytic Methods

The epoxy number was determined by titrating a sample with a dioxane solution of hydrochloric acid.¹⁶ The acid number was determined by titrating a sample dissolved in 20 cm³ DMSO and 5 cm³ H₂O with 0.1M NaOH. Ionic chlorine was determined by potentiometric titration with a 0.01M aqueous solution of AgNO₃. Elemental analysis of the products (C, H, N, S) was performed using an EA-1108 (FISONS, Italy) ana-

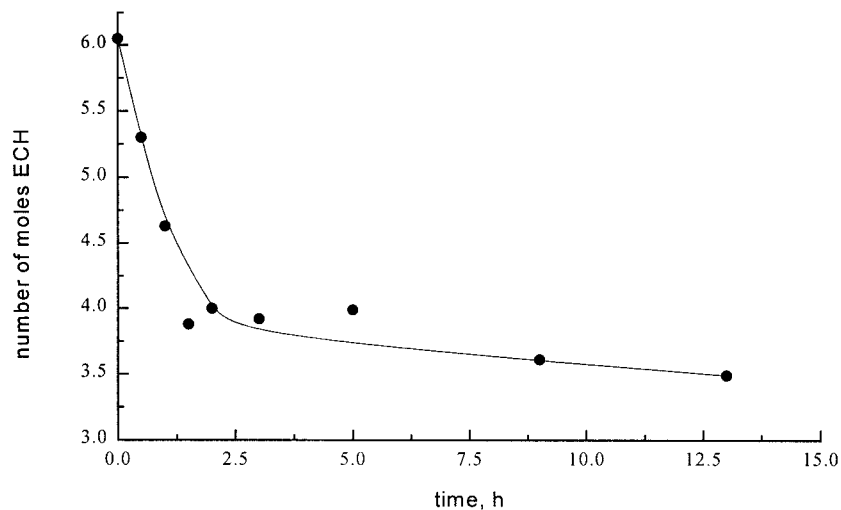
lyzer. Infrared spectra were recorded on an FTIR PARAGON 1000 spectrometer (Perkin-Elmer). The samples had the form of capillary films. ¹H-NMR spectra were recorded on an 80-MHz BS-586A spectrometer (Tesla, Czechoslovakia). The solvent was *d*₆-DMSO with the HMDSO internal standard. Thermal analysis of the products was carried out using a derivatograph (MOM, Hungary) in a nitrogen atmosphere. Two hundred milligrams of the sample was heated in a china crucible over the temperature range 20–1000°C. The sensitivity of the instrument was 1/10 for DTA and 1/10 for DTG. Some other properties of the products such as the refractive index, density (pycnometrically), viscosity (Höpler viscometer), and surface tension (torsion balance method) were evaluated in the temperature range 20–80°C.

RESULTS AND DISCUSSION

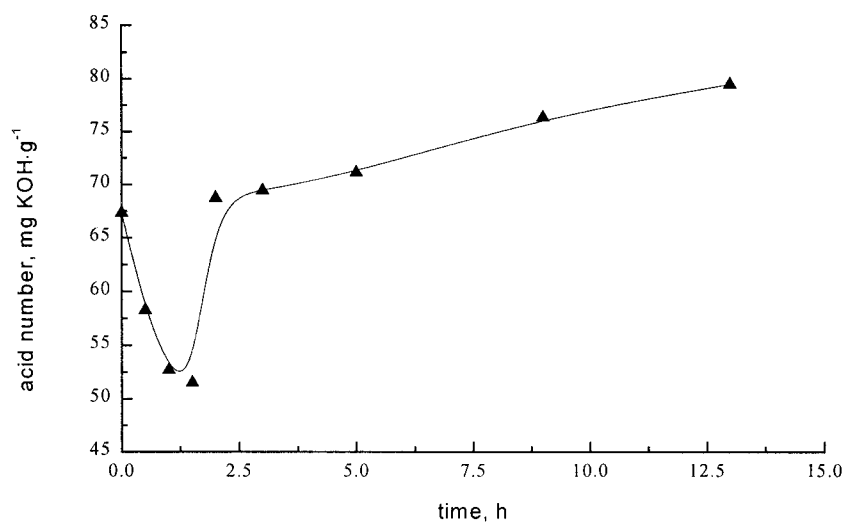
Reactions of TTCA with an excess of ethylene oxide or propylene oxide were carried out in DMF solutions in the presence of triethylamine as a catalyst. After the solvent and catalyst was removed under reduced pressure, resinous products

Table I Acid Numbers of Reaction Mixtures, Determined at $t = 0$ h

Molar Ratio TTCA : ECH	Acid Number (mg KOH g ⁻¹)	n_{SH} (mol)
1 : 1	93.02	1.80
1 : 2	88.41	1.85
1 : 3	76.69	1.74
1 : 6	67.31	1.86



(a)



(b)

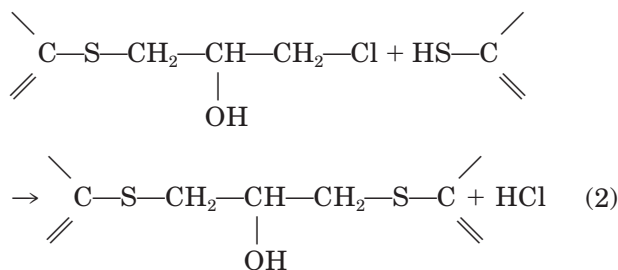
Figure 1 (a) Consumption of ECH and (b) change of the acid number in a reaction with TTCA. Molar ratio ECH:TTCA = 6; solvent, DMSO; $t = 60^{\circ}\text{C}$.

were obtained.¹ Reactions of TTCA with ECH, carried out under analogous conditions, gave no expected polyetherols. Crosslinking of the products occurred during the reaction. The most prob-

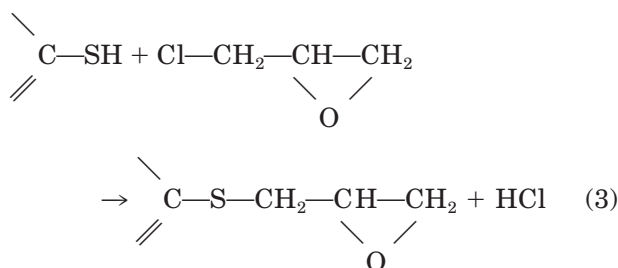
able reason was the consecutive reaction of chlorine substitution in the chlorohydroxypropyl derivative by the sulfur atom of a thiolic group in another TTCA acid molecule:

Table II Conditions at Which the Addition of TTCA to ECH Were Carried Out

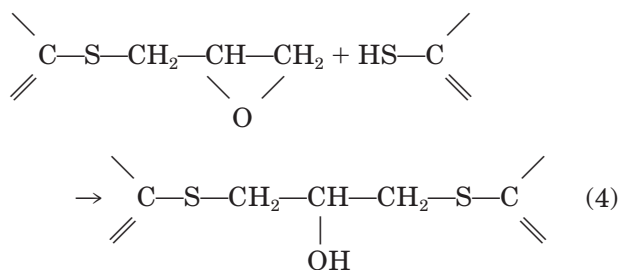
Molar Ratio TTCA : ECH	Temperature (°C)	Time (h)
1 : 6	80–100	10
1 : 9	80–100	21
1 : 12	80–100	37



Furthermore, because of the strong nucleophilic character of sulfur atoms, the possibility of the substitution of chlorine into the ECH molecule cannot be excluded either:



followed by the reaction of a thiolic group with the substitution of the product:



Dissolution of TTCA in DMF (or in DMSO) shifts the tautomeric equilibrium from the triketo form (dominating in the solid-state acid¹⁷) toward the dithiol form of TTCA, as revealed by the acid number measured just after combining the components (Table I). The large concentration of thiolic groups favors crosslinking, according to reactions (2) and (4). It appears that, in the reaction of 1 mol of TTCA with 6 mol of ECH in a DMSO solution, the acid number of the reaction mixture rapidly increased after 2 mol of oxirane had reacted (Fig. 1), suggesting that hydrochloride is released according to reactions (2) and (3). At the same time, the viscosity of the reaction mixture rapidly increases and then the system eventually gels. Hence, the reaction of TTCA with ECH was studied at the temperature of 60°C, because at the temperature of 100°C (applied in reactions with ethylene oxide or propylene oxide¹), crosslinking proceeded too quickly. It is noteworthy that increase of the acid number and gelation was not observed in reactions of TTCA with propylene oxide.¹⁸

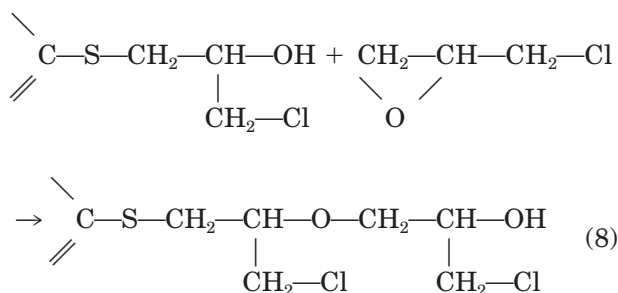
To prevent crosslinking, further reactions were carried out without a catalyst or diluent. The acid was mixed directly with ECH. In the beginning, the process was conducted in a heterogeneous system (until the thiolic-rich form of TTCA was reached). Then, the TTCA dissolved (or, strictly speaking, the —SH groups reacted) and the reac-

Table III Elemental Analysis of the Products of Reaction Between TTCA and ECH

Molar Ratio TTCA : ECH	Elemental Analysis							
	C (wt %)		H (wt %)		N (wt %)		S (wt %)	
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
1 : 6	34.44	34.17	4.54	4.50	5.74	5.28	13.13	14.17
1 : 9	35.68	32.43	4.79	4.87	4.16	4.34	9.52	9.65
1 : 12	36.38	34.77	4.93	5.08	3.26	2.65	7.47	7.55

Table IV Some Physical Properties of the Products of Reaction Between TTCA and ECH

Molar Ratio TTCA : ECH	Temperature (°C)	Refraction Index	Density (g cm ⁻³)	Viscosity × 10 ³ (Pa s)	Surface Tension × 10 ³ (N m ⁻¹)
1 : 6	20	—	—	—	—
	30	—	—	—	—
	40	—	—	—	—
	50	1.5587	1.4312	14,876	60.9
	60	1.5561	1.4209	6554	57.6
	70	1.5523	1.4117	3526	49.6
	80	1.5489	1.4034	1847	46.8
1 : 9	20	1.5515	1.4405	—	54.6
	30	1.5474	1.4311	19,095	48.4
	40	1.5439	1.4212	6738	45.8
	50	1.5403	1.4121	2727	42.3
	60	1.5366	1.4037	1314	39.6
	70	1.5321	1.3940	697	39.3
	80	1.5288	1.3843	392	38.5
1 : 12	20	1.5424	1.4279	17,759	46.3
	30	1.5389	1.4199	7651	43.8
	40	1.5352	1.4105	2677	39.4
	50	1.5318	1.4015	1273	36.3
	60	1.5278	1.3919	639	27.6
	70	1.5237	1.3814	354	25.3
	80	1.5202	1.3720	205	22.9



The amount of ionic chlorine found in the products (below 0.50%) and the results of elemental analysis (Table III) seem to confirm the reaction scheme described above. The total amount of chlorine tallied with that calculated from the mass balance (e.g., in the product of reaction of 1 mol of TTCA with 6 mol of ECH: % Cl_{det} = 28.65 and % Cl_{calc} = 29.09).

The final product of the reaction is a mixture of chlorohydroxyalkyl derivatives of TTCA and 1,3-dichloropropan-2-ol (glycerol dichlorohydrine), as follows from the proposed reaction schemes. The last compound was isolated by distillation under reduced pressure from the final reaction mixture. Its ¹H-NMR spectrum is presented in Figure 2.

The structure of the products was determined by IR and ¹H-NMR techniques. In the IR spectra of TTCA derivatives prepared in reactions with ECH (Fig. 3), bands analogous to those found in the spectra of products of TTCA addition to ethylene (propylene) oxide have been identified (see Fig. 2 in ref. 1). Somewhat stronger absorption of the *s*-triazine ring band at 760 cm⁻¹ with overlapping C—Cl stretching vibrations was observed. In the ¹H-NMR spectra of the derivatives, bands analogous to those in the spectra of products of TTCA addition to ethylene (propylene) oxide have been identified as well (see Fig. 4 in ref. 1). The extra signal due to chloromethyl groups overlaps with a signal in the range of 2.7–3.8 ppm.

Certain physical properties of the products were determined, such as the refractive index, density, viscosity, and surface tension (Table IV). Typical dependencies of these properties on the temperature were observed. Thermal analysis of the polyetherols shows that the products of the reaction of TTCA with ECH are quite resistant to thermal treatment, similarly to the adducts with ethylene oxide or propylene oxide.¹

CONCLUSIONS

The reactions of TTCA with ECH should be carried out without a catalyst (triethylamine) or a solvent (DMF, DMSO). Their presence in the reaction mixture leads to undesirable crosslinking of the mixture. The reaction of the addition of TTCA to epoxy groups is accompanied by the substitution of chlorine in ECH by sulfur from the thiolic group of the acid. The hydrochloride released reacts with the product of substitution or with unreacted ECH. This is the reason why the products contain a small amount of 1,3-dichloropropan-2-ol.

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