山形大学紀要(工学) Bull. Yamagata Univ.(Eng.) Vol. 19 No. 2 Jan. 1987

Reaction of Tetrahydrofuran and Acetic Anhydride Catalyzed by Electrogenerated Acid

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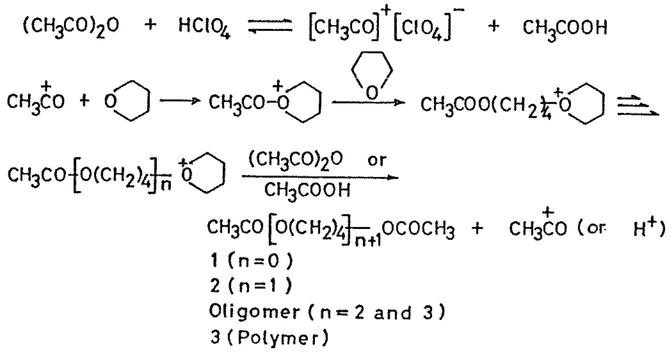
Abstract

The anodic oxidation of tetrahydrofuran with acetic anhydride and lithium perchlorate undergoes the ring opening reaction catalyzed by electrogenerated acid to yield diacetates of 1, 4−butanediol, 4, 4'−oxybis (1 −butanol) and α−hydro−ω−hydroxy−poly (oxytetramethylene). The distribution of these products depends on the quantity of acetic anhydride and the electrogenrated acid foromed during the progress of electrolysis.

Introduction

An acidic species is usually formed in anolyte during the progress of electrolysis and has been recently applied to acid−catalyzed reactions as an electrogenerated acid (EGA), which is considered to be a perchloric acid in the electrolysis using perchlorate as a supporting electrolyte. For example, the anodic oxidation of tetrahydrofuran (THF) containing perchlorate initiates cationic polymerization by the EGA. [1)]

On the other hand, it has been reported that the acetyl cation formed by addition of perchloric acid to a mixture of THF and acetic anhydride is also effective for the cationic polymerization of THF to yield α−hydro−ω−hydroxy−poly (oxytetramethylene) diacetate **3** as the following scheme. [2, 3)]



Since the same reaction as that shown by the above scheme could be expected to take place when an acetic anhydride was added to the anolyte in an electrolysis of THF with perchlorate, we have tried to confirm the effect of the acetic anhydride as an additive on the anodic reaction of THF.

Experimental

Tetrahydrofuran, acetic anhydride and lithium perchlorate were purified and dried by usual methods. A typical electrochemical reaction is as follows. A mixture of THF and acetic anhydride (~30cm^3) containing 0.5 mol dm^{-3} $LiClO_4$ was placed in an anode chamber (catholyte : THF solution of 0.5 mol dm^{-3} $LiClO_4$) followed by the electrolysis for a given quantity of electricity under the following conditions : anode and cathode, platinum plate (7.5cm^2); current, 0.3 A (0.04 A cm^{-2}); temperature, room temperature.

After the electrolysis, the anolyte was allowed to stand for 10 hours and then water (300cm^3) was added to the reaction mixture. The resulting precipitate from the aqueous solution was identified as **3** by comparing ir spectrum with that of the authentic sample obtained by the chemical polymerization of THF initiated by acetic anhydride and perchloric acid. The average molecular weight was over 2×10^3 in every case.

Other two compounds were isolated by distillation of ether-extract from the aqueous anolyte after the precipitation of polymer. Diacetates of 1, 4 −butanediol (**1**, n= 0 in the above reaction scheme) and 4, 4'−oxybis (1 −butanol) (**2**, n= 1) were obtained with a small amount of oligomer (n= 2 and 3). **1** : bp 130℃ (21mm Hg); IR (CCl_4) 1046, 1232 and 1740cm^{-1}; Mass m/e 174 (M^+); ^1H−NMR (CCl_4) δ 1.51~1.70 (m, 4 H), 1.95 (s, 6 H) and 3.95~4.11 (m, 4 H). **2** : bp 160℃ 21 mm Hg); IR (CCl_4) 1065, 1110, 1230 and 1740 cm^{-1}; Mass m/e 246 (M^+); ^1H−NMR (CCl_4) δ 1.51~1.71 (m, 8 H), 1.96 (s, 6 H), 3.23~3.44 (m, 4 H) and 3.94~4.12 (m, 4 H).

The yields of **1** and **2** were determined by a gas chromatography under the following conditions : column packing, Triton X−305; carrier gas, N_2 (30cm^3 min^{-1}); temperature, 180℃. Oligomer was not isolated but gave two peaks at longer retention times than that of **2** in the chromatogram. The yield estimated was less than 5 % even in the highest one.

The chemical reactions were carried out as follows. A 70% perchloric acid was added to a mixture of THF and acetic anhydride, and then the mixture was allowed to stand for 10 hours, followed by the quantitative analyses of products in a similar manner as above.

Results and Discussion

The electrochemical results are summarized in Table 1. As shown in the table, the only polymer **3** was obtained on addition of a catalytic amount of acetic anhydride (run 1). At an increased amount of acetic anhydride, **1** and **2** were mainly formed with trace amounts of oligomer and polymer for the electrolysis at the same electricity as that of run 1 (runs 3 and 4). The formation of **2** is one of features in these electrochemical reactions. It is therefore expected that the electrolysis becomes a useful method for the preparation of **2** by selection of the proper experimental conditions. However, the yield of **2** was not so high at a molar ratio (THF/Ac_2O) of 2, because a considerable amount of THF remained unreacted (run 3). Furthermore, the total yields of **1** and **2** increased at the molar ratio of 0.3, but the selectivity of **2** became poorer (run 4).

The attempts to enhance the yield and selectivity of **2** were therefore made by alternation in the electrolytic conditions. When sodium acetate was added to the anolyte under the same conditions as those of runs 3 and 4, the formation ratio of **2** to **1** increased without variation in the total yields of **1** and **2** compared with runs 3 and 4 (runs 5 and 6). However, the increase in an amount of sodium acetate resulted in no reaction (run 7). It is considered that sodium acetate neutralized the formed EGA to decrease the concentration in anolyte and caused no reaction by adding it over a quantity of the EGA formed by electrolysis. The quantity of EGA appears to play

Table 1 The effects of acetic anhydride and electricity on electrolysis of THE with perchlorate

Run	Anolyte				Electricity passed (C)	Yield of products(%)			
	THF (mol)	Ac_2O (mol)	AcONa (mol)	Molar ratio of THF/Ac_2O		**1**	**2**	Oligomer	polymer
1	0.60	0.012	0	50	2120*1	0	0	0	65
2	0.60	0.06	0	10	2120	trace	trace	trace	55
3	0.30	0.15	0	2.0	2120	30	16	trace	trace
4	0.12	0.40	0	0.3	2120	70	5	trace	trace
5	0.30	0.15	0.013	2.0	2120	21	23	< 5	trace
6	0.12	0.40	0.013	0.3	2120	27	54	< 5	trace
7	0.12	0.40	0.13	0.3	2120	0	0	0	0
8	0.12	0.40	0	0.3	1060*2	28	60	< 5	trace
9	0.12	0.40	0	0.3	580*3	23	65	< 5	trace
10	0.10	0.50	0	0.2	1060	32	54	< 5	trace
11	0.10	0.50	0	0.2	580	35	51	< 5	trace

Ac_2O : acetic anhydride, AcONa : sodium acetate
*1 : 0.22F *2 : 0.011F *3 : 0.006F

an important role for the formation of **2**. Therefore, we tried the electrolyses under the conditions of lower electricity than those of runs 1 and 6.

If one mol of EGA is formed by one-electron transfer, the formed EGA is 0.022 moles in runs 1 ~ 6 and hence 0.09 moles of the EGA is supposed to be effective for the reaction in the presence of 0.013 moles sodium acetate. As expected, the yield of **2** resulted in 60~65% with decreasing an electricity without adding sodium acetate (runs 8 and 9). The electrolyses were further tried under the various conditions, but no better results than that of run 9 were obtained (runs 10 and 11).

Shono et al. have reported the polymerization initiated by acetic anhydride and perchloric acid to give the polymer **3**.[2] In their experiments, **2** was isolated by distillation from a liquid product of low viscosity, though no quantitative results were described in detail. The same reaction was traced and gave **2** in a yield of about 10% with **1** and **3**.

In addition, some reactions were carried out by adding a 70% perchloric acid instead of EGA to the solution at the same composition as that of the anolyte without perchlorate, and the results are shown in Table 2. In any case, **2** was formed with **1**, but the yield of **2** was 10% even in the highest one (runs 1 ~ 3). Since the water involved in the 70% perchloric acid was considered to influence the reaction, the *in situ* dehydration method reported previously by us[1] was applied to this reaction by adding maleic anhydride to the reaction mixture (run 4). However, no remarkable effect of maleic anhydride on the yield was observed, though there was a slight increase in the total yield of **1** and **2**.

Consequently, the higher yield and selectivity of **2** to **1** are a characteristic in electrochmical reaction and could be briefly explained as follows. The electrochemical reaction proceeds in the vicinity of electrode surface *via* adsorbed cationic species and hence the chemical reaction in the bulk of anolyte may specify the products by the contribution of diffusion to the bulk in higher quantity of EGA. Accordingly,

Table 2 The reactions of THF and acetic anhydride in the presence of perchloric acid

	Reaction mixture					Yield of products (%)			
Run	THF (mol)	Ac_2O (mol)	MA (mol)	Perchloric acid (mol)	Molar ratio of THF/Ac_2O	**1**	**2**	Oligomer	Polymer
1	0.30	0.45	0	0.022	2	37	10	trace	trace
2	0.12	0.40	0	0.011	0.3	62	8	< 5	trace
3	0.12	0.40	0	0.006	0.3	65	10	< 5	trace
4	0.12	0.40	0.01	0.006	0.3	60	15	< 5	trace

MA : maleic anhydride

the product distribution is similar to that in the chemical reaction of THF, acetic anhydride and perchloric acid.

In the case of lower quantity of EGA, products **1** and **2** could be derived from the adsorbed cationic species($CH_3CO\{O(CH_2)_4\}_n\overset{+}{O}$⬠), which exists mainly as n = 0 and 1 to yield **1** and **2** by the reaction with acetic anhydride. The higher selectivity or **2** to **1** must be discussed by considering kinetically the reaction of the cation with THF and acetic anhydride on the anode, and a further study is now in progress on the basis of electrochemical measurements.

References

1) M. Sugawara and H. Kamata, *Bull. Yamagata Univ.* (*Eng.*), **19** (1), 57 (1986) and references therein.

2) T. Shono, T. Tsujino and Y. Hachihama, *Kogyo Kagaku Zasshi*, **61**, 1347 (1958).

3) H. Meerwein, D. Delfs and H. Morschel, *Angew. Chem.*, **72** 927 (1960).