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INFLUENCE OF REACTION CONDITIONS ON MAIN AND SIDE REACTIONS DURING THE TRANSESTERIFICATION OF DIMETHYL TEREPHTHALATE WITH 1,4-BUTANEDIOL

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ABSTRACT

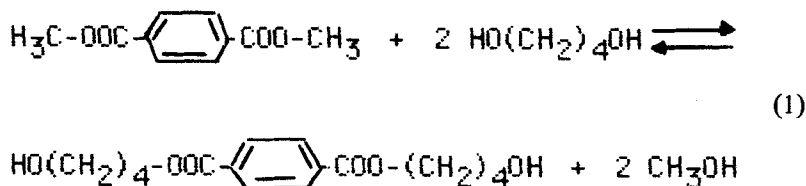
The transesterification of dimethyl terephthalate (DMT) with 1,4-butanediol (BD) has been studied by measuring the amount of methanol and tetrahydrofuran formed during the reaction. Investigation of various catalyst systems revealed that titanium isopropoxide was a better catalyst than conventional transesterification catalysts such as manganese and cobalt acetates. Increases in the temperature, BD/DMT ratio, and catalyst concentration led to higher production of methanol. Increases in temperature and BD/DMT ratio raised THF production, but increased catalyst concentration decreased the amount of THF produced. The relative importance of BD dehydration and cyclization of 4-hydroxybutyl ester end groups in the formation of THF was also studied.

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INTRODUCTION

Poly(1,4-butylene terephthalate) (PBT) is produced by polycondensation of bis(4-hydroxybutyl) terephthalate (BHBT) or its oligomers. Although BHBT can be synthesized both by transesterification of dimethyl terephthalate (DMT) and 1,4-butanediol (BD) and by direct esterification of BD and terephthalic acid (TA), the substantial proportion of BD converted to tetrahydrofuran (THF) during esterification makes the former process more advantageous.

The transesterification reaction may be represented by



This reaction is always accompanied by the formation of THF.

Unlike the transesterification of DMT with ethylene glycol, very few studies related to the transesterification of DMT with BD have been reported in the literature [1-3]. Sivaram and coworkers [1] studied the performance of various catalysts, finding that titanium derivatives, in particular titanium isopropoxide, appear to be better catalysts than calcium acetate. Also, they observed that increased reaction time, higher temperatures, and larger stoichiometric excess of BD led to an increase in THF formation. Since the aim of Sivaram and coworkers [1] was to synthesize BHBT in its pure monomeric form, they did not carry out the reactions under industrial conditions but with a very high BD/DMT ratio (6/1). Padias and Hall [2] reported that with no catalyst, no THF was produced by heating BD for 8 h at 210°C. These authors proposed that, during the esterification of TA and BD, THF could be produced by both BD dehydration catalyzed by acid groups and from hydroxybutyl end groups. Pilati et al. [3] found that the production of THF was enhanced by the presence of benzoic acid.

In the present work, transesterification of DMT with BD was carried out in the presence of various catalyst systems. The influence of temperature, BD/DMT ratio, and catalyst concentration on both the BHBT production rate and the formation of THF were investigated.

EXPERIMENTAL

Reactions were carried out in standard reaction equipment provided with a rectification column and mechanical agitation. DMT (0.5 mol) was introduced into the reaction vessel and electrically heated to its melting point ($\sim 140^\circ\text{C}$). Then BD and the catalyst were added and the reaction mixture heated until the temperature reached its final value. The internal reactor temperature was continuously measured and recorded. A controlled stream of nitrogen flowed through the reaction vessel to help removal of methanol and THF. Methanol and THF were collected in a cold trap. The temperature of the effluent in the cold trap was measured in order to determine the amount of methanol and THF not retained in the trap. The amounts of methanol and THF collected in the trap were measured by gravimetry and gas chromatography using a Carbowax-400 column, 2 m in length, at 50°C .

Catalyst concentration is expressed as wt% based on DMT, i.e., (weight of catalyst $\times 100$)/(weight of DMT).

RESULTS AND DISCUSSION

The influence of the catalyst system, temperature, BD/DMT ratio, and catalyst concentration on the BHBT and THF production rates was investigated.

Effect of the Catalyst System

Figure 1 shows the effect of the nature of the catalyst both on the rate of transesterification of dimethyl terephthalate with 1,4-butanediol and on the rate of formation of THF for the three catalysts used in this work: manganese acetate [MnAc; $(\text{CH}_3\text{COO})_2\text{Mn}\cdot 4\text{H}_2\text{O}$], cobalt acetate [CoAc; $(\text{CH}_3\text{COO})_2\text{Co}\cdot 4\text{H}_2\text{O}$], and titanium isopropoxide [$\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$]. The extent of transesterification is given in terms of moles of methanol produced. The results show that titanium isopropoxide gave higher transesterification rates and lower production of THF than the acetates. Additionally, cobalt acetate gave a slight color to the final product.

The existence of a possible catalytic synergy between titanium isopropoxide and manganese acetate was explored by carrying out transesterifications with mixtures of both catalysts at constant total amount of catalyst. It can be seen in Fig. 2 that, when the fraction of titanium isopropoxide in the catalyst mix-

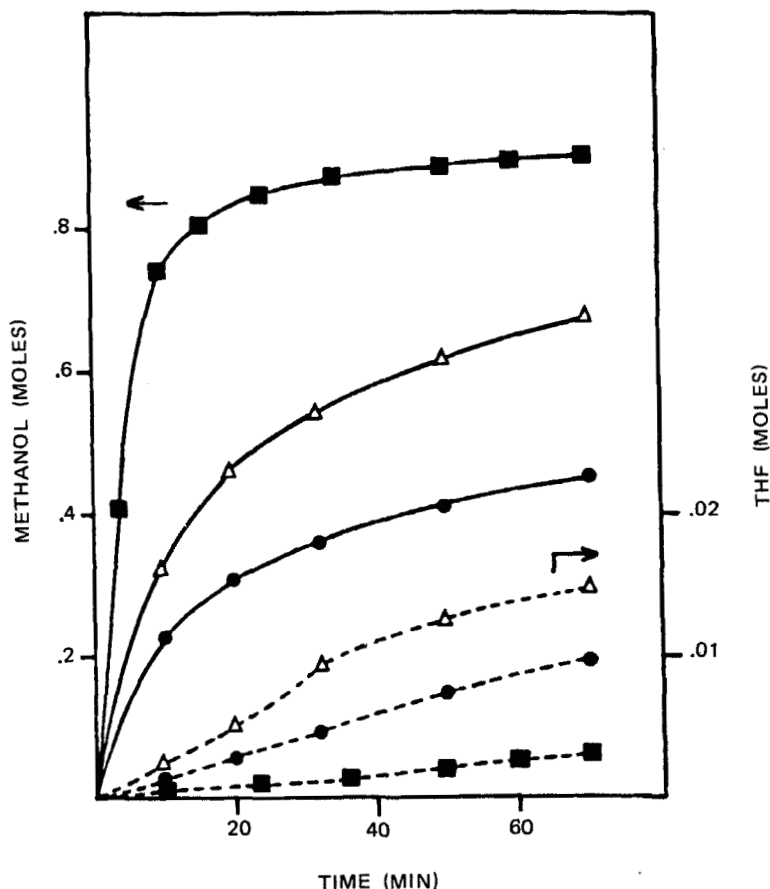


FIG. 1. Effect of the type of catalyst. DMT = 0.5 mol; BD/DMT = 2; $T = 200^{\circ}\text{C}$. (■) Titanium isopropoxide, 0.16 wt%; (△) CoAc, 0.16 wt%; (●) MnAc, 0.17 wt%. Solid lines, methanol production; dashed lines, THF production.

ture is low, a small increase produces a great increase in the extent of reaction, whereas when the fraction is higher than 20%, the system is very insensitive to variations of the titanium isopropoxide content. However, this behavior should not be attributed to synergy but, as it will be shown later, to a catalyst concentration effect.

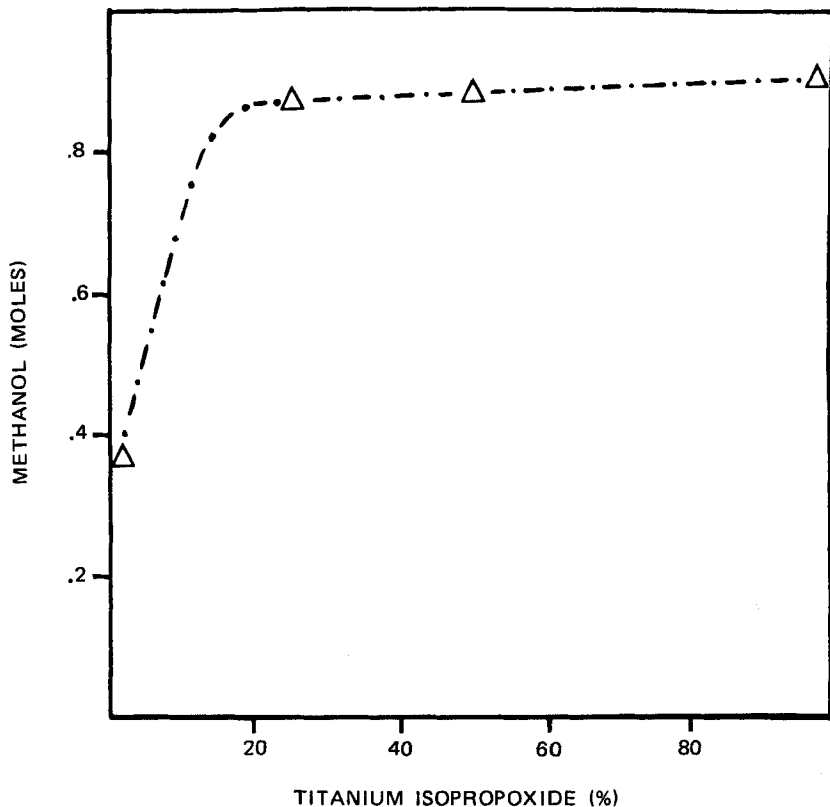


FIG. 2. Effect of the ratio of titanium isopropoxide to manganese acetate. Reaction time, 36 min; DMT = 0.5 mol; BD/DMT = 2; $T = 200^{\circ}\text{C}$; total amount of catalyst, 0.16 wt%.

Effect of BD/DMT Ratio

In order to investigate the effect of the BD/DMT ratio on the transesterification and side reactions, experiments with different BD/DMT ratios were carried out with titanium isopropoxide as catalyst. In these reactions the amounts of DMT (0.5 mol) and catalyst (0.16% w/w DMT) were kept constant. The results are presented in Fig. 3, where it can be seen that an increase of the BD/DMT ratio led to a higher transesterification rate, but also more THF was produced.

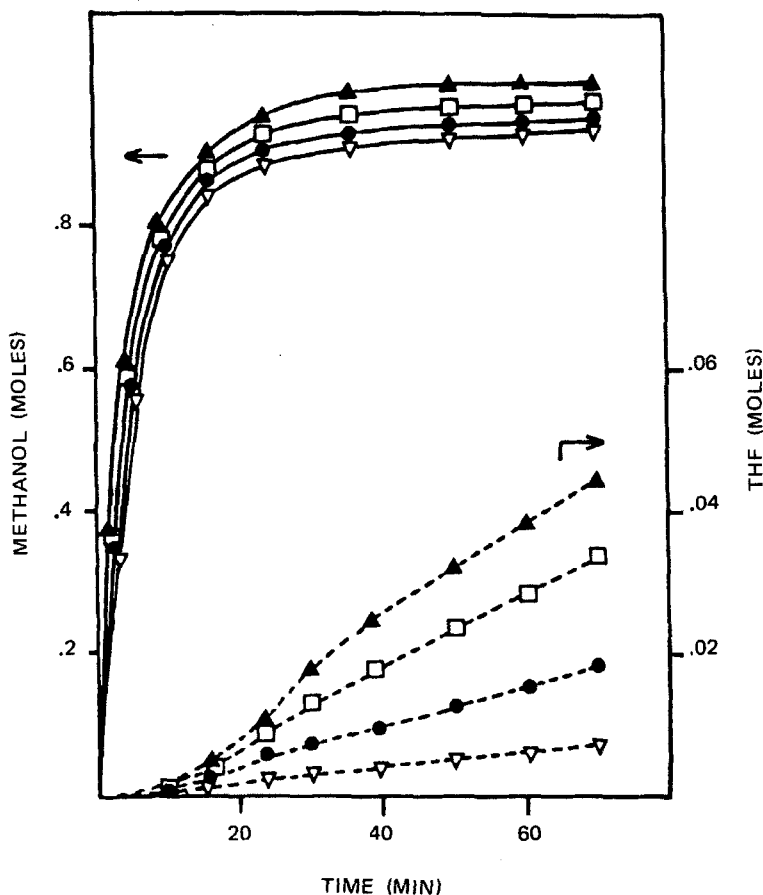


FIG. 3. Effect of the BD/DMT ratio. DMT = 0.5 mol; titanium isopropoxide = 0.16 wt%; $T = 200^{\circ}\text{C}$. BD/DMT: (▽) 2; (●) 3; (□) 4; (▲) 5.

Effect of Temperature

Because of the way in which reactions were carried out, transesterification was not an isothermal process, but the temperature initially increased, and only after 20 min was a constant temperature reached. Figure 4 shows the effect of the temperature on the production of BHBT and THF, and it can be seen that the higher the temperature, the greater the production of BHBT and THF.

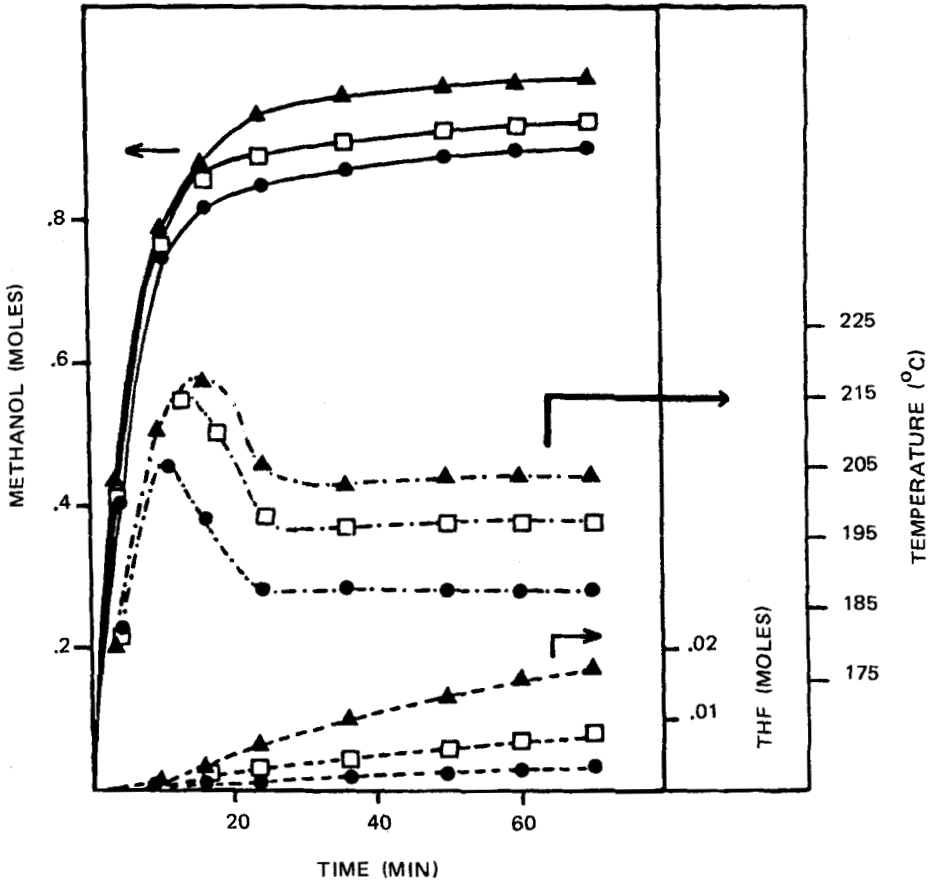


FIG. 4. Effect of the temperature profile. DMT = 0.5 mol; BD/DMT = 1; titanium isopropoxide = 0.16 wt%.

Effect of Catalyst Concentration

The effect of catalyst concentration on the production of methanol and tetrahydrofuran is presented in Fig. 5, which shows that at low catalyst content both reaction rates were very sensitive to variations in the catalyst concentration. In contrast, when the catalyst content was high, the system appeared to be almost insensitive to changes in catalyst concentration. This

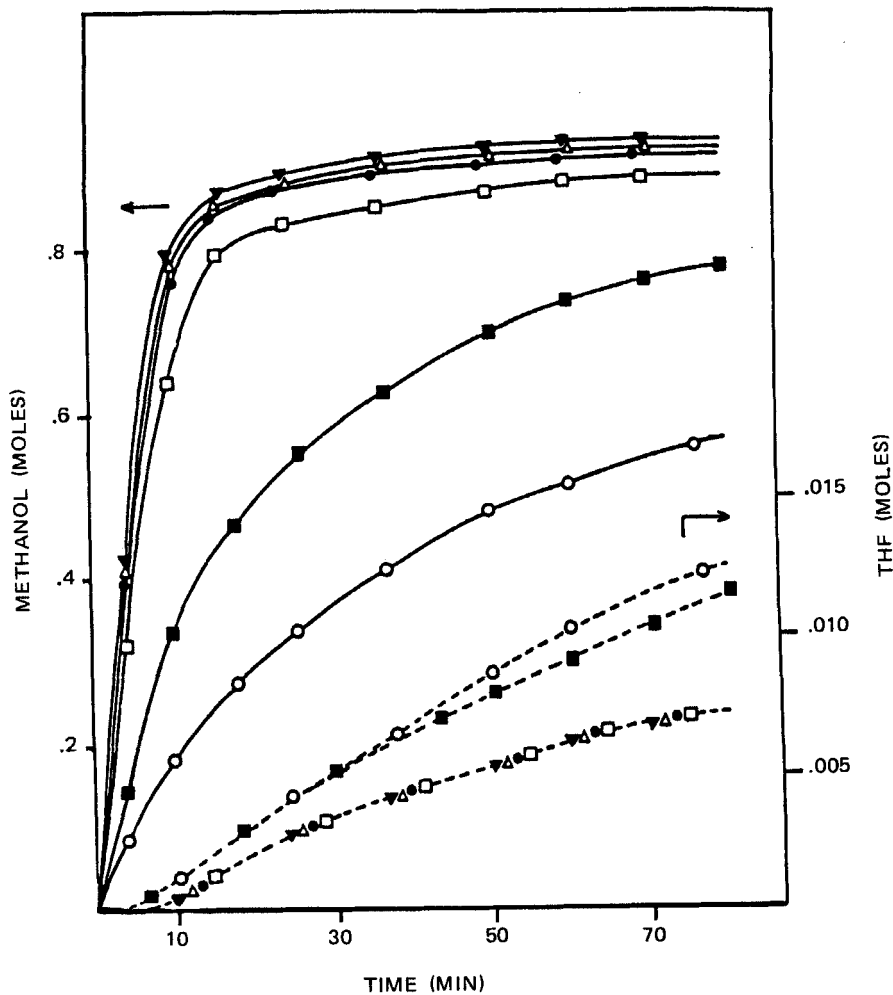


FIG. 5. Effect of the catalyst concentration. DMT = 0.5 mol; BD/DMT = 2; $T = 200^{\circ}\text{C}$. Titanium isopropoxide (wt%): (\blacktriangledown) 0.26, (\triangle) 0.199, (\bullet) 0.16, (\square) 0.058, (\blacksquare) 0.009, (\circ) 0.00056.

behavior is similar to the one found for the transesterification of DMT and ethylene glycol [4].

Figure 6 shows the effect of catalyst concentration on the amounts of methanol and THF produced up to a given reaction time. It may be seen

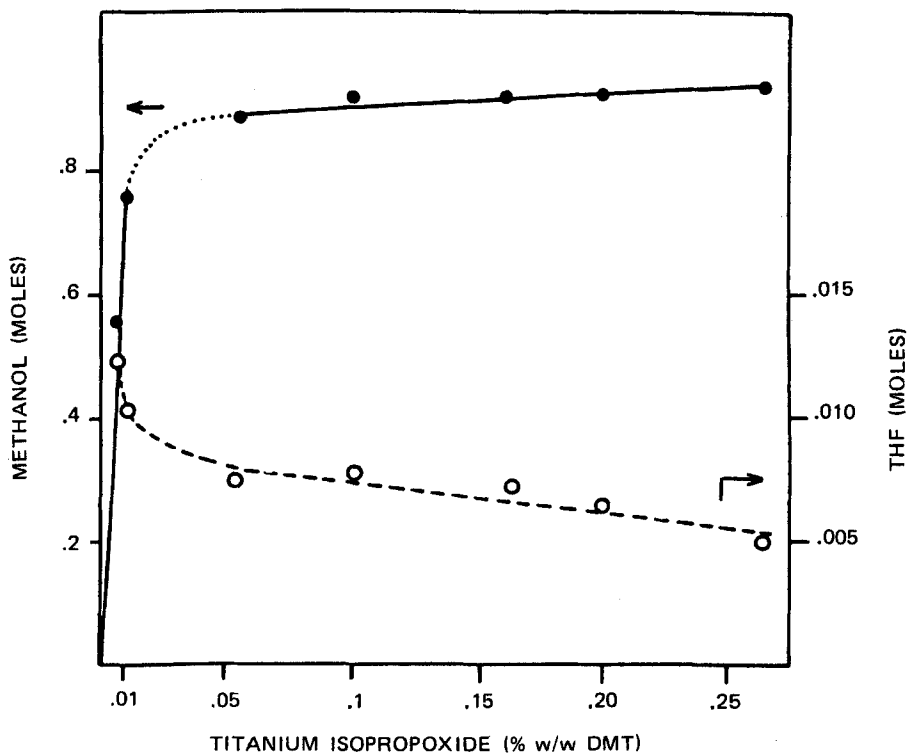
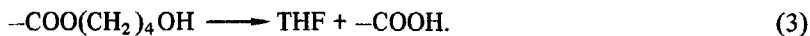


FIG. 6. Effect of the catalyst concentration on the amount of methanol and THF produced up to a reaction time of 70 min. DMT = 0.5 mol, BD/DMT = 2, $T = 200^{\circ}\text{C}$.

that, when more methanol is formed, less THF is produced. This suggests that THF is mainly formed from BD through a dehydration reaction because when the extent of the reaction is low, there is more BD available for dehydration. This hypothesis will be considered more fully in the next section.

Side Reactions: THF Production

According to previous authors [2, 3], THF may be formed through the following reactions:



The relative importance of Reactions (2) and (3) can be estimated by analyzing the kinetic results presented in the previous sections.

Reaction (2) would be promoted by increasing BD concentration, whereas Reaction (3) would be favored by increasing hydroxybutyl and groups concentration, namely the amount of methanol produced. Figure 3 shows that an increase in the BD/DMT ratio leads to a significant increase in the production rate of THF. An examination of the methanol curves shows that such an increase in THF formed could not be attributed to higher concentration of hydroxybutyl end groups. It might therefore be concluded that, for high BD/DMT ratios, the formation of THF takes place mainly through Reaction (2). The results in Fig. 6 show that this conclusion may be extended to a BD/DMT ratio of 2, which seems to be in disagreement with the results in Figs. 4 and 5 where almost no decrease of THF production rate with increasing BD conversion was observed. However, both results may be explained by taking into account the catalytic effect of acid groups on the dehydration of BD [2, 3]. Thus, high production rates of THF would be obtained at high concentrations of either BD or acid groups. During the reactions, the concentration of BD decreased monotonically whereas that of acid groups increased continuously. The absence of acid groups could explain the low THF production rate obtained at the beginning of some reactions, while the subsequent increase of such a reaction rate would be associated with an increase in acid groups concentration. Additionally, this increase in the concentration of acid groups would counteract the decrease of BD concentration, leading to an almost constant production rate of THF.

CONCLUSIONS

It has been shown that titanium isopropoxide is a better catalyst than conventional transesterification catalysts such as manganese and cobalt acetates. No catalytic synergy between titanium isopropoxide and manganese acetate was found. An increase in the temperature, BD/DMT ratio, or catalyst concentration led to higher methanol production. The same behavior with respect to temperature and BD/DMT ratio was followed by THF production, but when catalyst concentration increased, the amount of THF produced decreased. The kinetic results indicated that the major part of the THF was produced through dehydration of BD catalyzed by acid groups.

ACKNOWLEDGMENT

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