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Cleavage of Dibenzyl Ether in the Presence of Zinc Halides

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The large amount of water liberated during coal liquefaction in the presence of $ZnCl_2$ is believed to derive from the cleavage of benzylic ethers. The details of this process have been studied using dibenzyl ether as a model structure and $ZnCl_2$, $ZnBr_2$, and ZnI_2 as catalysts. The influence of H_2O and HX on the progress of the reaction was also examined. In the absence of HX addition, ZnX_2 activates the ether by forming a Lewis acid–base complex with it. Water interferes with the formation of this complex by competing for ZnX_2. In the presence of HX, an adduct is formed, $HX \cdot ZnX_2$, that is much more active catalytically than ZnX_2. The presence of water does not influence the activity of the Brønsted acid form of the catalyst. Activation of dibenzyl ether is achieved by protonation of the ether. The relative activity of the zinc halides depends on which of the two forms is present. If anhydrous ZnX_2 is the catalyst, the activity decreases in the order $ZnCl_2 > ZnBr_2 > ZnI_2$. On the other hand, if $HX \cdot ZnX_2$ is the prevalent form, the activity decreases in the order $HI \cdot ZnI_2 > HBr \cdot ZnBr_2 > HCl \cdot ZnCl_2$. It is observed that during the reaction of dibenzyl ether in the presence of ZnX_2, a small amount of HX is liberated, which then combines with ZnX_2 to form $HX \cdot ZnX_2$. Because the Brønsted acid form of the catalyst is more active than the Lewis form, the apparent activity of the catalyst increases after a period of induction during which HX is generated.

INTRODUCTION

Zinc halides, and in particular $ZnCl_2$, are active catalysts for the liquefaction of coal (*1–4*). One of the processes promoted by these materials is the cleavage of ether linkages between aromatic centers. The large amount of water liberated during coal liquefaction under the influence of $ZnCl_2$ is believed to derive from the cleavage of benzylic ethers. In an effort to determine the extent to which $ZnCl_2$ catalyzes the cleavage of ether linkages, Mobley and Bell (*5, 6*) investigated the reactions of several ethers containing phenyl, benzyl, and naphthyl groups, as well as cyclic ethers. Their work demonstrated that complete elimination of oxygen to form water was achieved with dibenzyl and cycloaliphatic ethers, but oxygen bonded directly to a phenyl or naphthyl group was converted to an unreactive phenolic hydroxyl group. More recently, Frederick and Bell (*7*) have carried out a study of the cleavage of benzylaryl ethers in the presence of $ZnCl_2$ and $ZnBr_2$. It was observed that while $ZnCl_2$ by itself is not an active catalyst, in the presence of HCl it forms a stable adduct which is highly active. While the structure of the adduct was not determined, it is postulated to be $HCl \cdot ZnCl_2$. $HBr \cdot ZnBr_2$ behaves in a similar manner to $HCl \cdot ZnCl_2$ but is tenfold more active. Cleavage of the ether always occurred at the oxygen–methylene bond. The observed reaction kinetics were well represented by a model based upon a carbocation mechanism of the cleavage process.

This paper presents the results of an investigation on the effects of $ZnCl_2$, $ZnBr_2$, and ZnI_2 on the reactions of dibenzyl ether. A major purpose of this effort was to identify the influence of catalyst composition and reaction conditions on the kinetics of ether cleavage. The influence of water and hydrogen halides on the progress of the re-

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action was also examined. The similarities and differences between the reactions of dibenzyl ether and benzylphenyl ether were also considered.

EXPERIMENTAL

Reactions were carried out in a 300-cm^3, 316-stainless-steel, stirred autoclave (Autoclave Engineers, Inc. Model ABP-300) fitted with a glass liner. A 30-cm^3, stainless-steel vessel was connected to the gas inlet line and to the autoclave. This vessel was used to hold a solution of the reactant prior to its injection into the autoclave. The temperature of the contents of the autoclave was monitored using a sheathed thermocouple and the pressure within the autoclave was measured using a Bourdon gauge. Liquid samples were taken through a ⅛-in. sampling tube which was cooled in an ice bath, after emerging from the autoclave.

A run was begun by sieving the dried catalyst and placing 5.0×10^{-3} mole of the 100/700 Tyler mesh (147–88 μm) cut in a glass liner, together with 50 ml of solvent. Any additional reactant or promoter was then injected into the glass liner using a microsyringe (Hamilton). This process was carried out in a nitrogen-purged dry box. The glass liner was quickly transferred to the autoclave, and the autoclave was sealed and flushed with nitrogen. The reactant was weighed in the dry box and dissolved in 20 ml of solvent. This solution was transferred to the reactant holding vessel, which was then flushed and pressurized with hydrogen. The autoclave was heated to 10 K above the desired reaction temperature, while the reactant-holding vessel remained at room temperature. The reactant solution was then injected into the autoclave with hydrogen. The autoclave temperature dropped 10 K immediately and was maintained at that temperature throughout the reaction. Liquid samples were taken as the reaction progressed.

Analysis of the liquid samples was carried out by gas chromatography using a 3 mm × 3 m, stainless-steel column packed with 5% OV-225 on Chromosorb P. Product identification was made using a Finnigan 4023 GC–MS and verified by matching peak retention times with those of pure components.

Dibenzyl ether (Aldrich), benzyl alcohol (Aldrich), and benzyl chloride (Aldrich) were used as reactants. Benzene (Mallinckrodt) and *p*-xylene (Mallinckrodt) were dried by refluxing under nitrogen in the presence of sodium. All reactants, solvents, and catalysts were stored in a dry box. The catalysts, $ZnCl_2$ (MCB), $ZnBr_2$ (MCB), and ZnI_2 (Fischer Scientific), were dried for 88 h at 383 K in a vacuum oven immediately prior to use.

In a number of the experiments, HCl was added to $ZnCl_2$. For this purpose, HCl was produced by the reaction of benzyl chloride with benzene during the heatup of the autoclave. The reaction was found to go to completion, and the amount of HCl produced was determined from the measured amount of diphenylmethane produced.

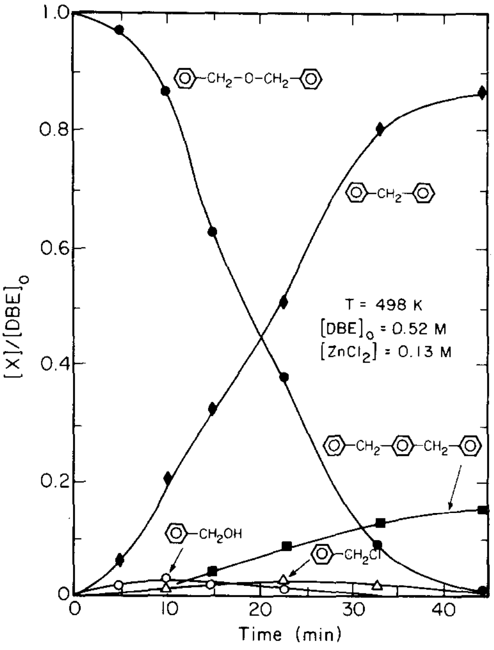

FIG. 1. Concentration versus time profiles for the reaction of DBE in the presence of $ZnCl_2$.

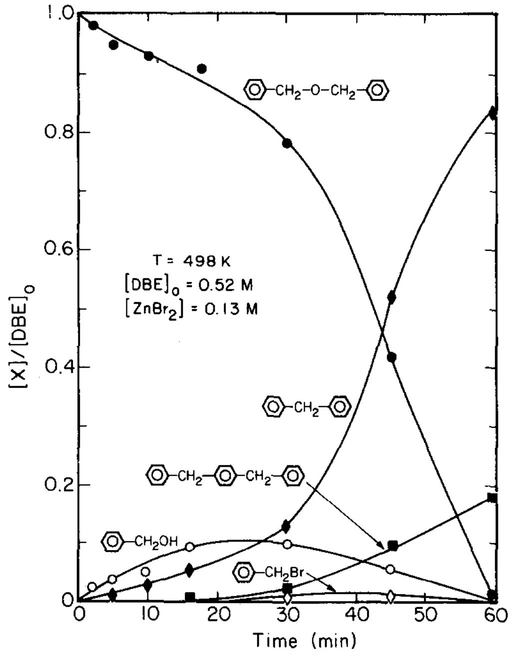

FIG. 2. Concentration versus time profiles for the reaction of DBE in the presence of $ZnBr_2$.

RESULTS

Figure 1 shows the variation in product concentrations with time observed during the reaction of dibenzyl ether (DBE) in the presence of $ZnCl_2$ at 498 K. The rate of DBE consumption is slow initially but then accelerates. Two intermediate products are formed, benzyl alcohol and benzyl chloride. The concentration of benzyl alcohol builds up rapidly and reaches a maximum at about 10 min. The concentration of benzyl chloride builds up more slowly and does not reach a maximum until 22 min. Diphenylmethane and dibenzylbenzene are observed as the final reaction products. At 100% conversion of DBE, the yield of these products is 85 and 15%, respectively. The three isomers of dibenzylbenzene appeared in the ratio *ortho* 30%, *meta* 20%, and *para* 50%.

Figures 2 and 3 show the concentration versus time curves for the reactions of DBE in the presence of $ZnBr_2$ and ZnI_2, respectively. The disappearance of DBE in the $ZnBr_2$-catalyzed reaction undergoes an induction period longer than that observed with $ZnCl_2$ as the catalyst and requires more time to reach 100% conversion. During the induction period, more benzyl alcohol and less diphenylmethane are found with $ZnBr_2$. The products with $ZnBr_2$ are the same as with $ZnCl_2$ except that benzyl bromide is produced rather than benzyl chloride. At long reaction times a small amount of toluene was also observed. The ZnI_2-catalyzed cleavage of DBE exhibits an induction period of duration comparable to that observed using $ZnBr_2$, but the rate of reaction during the subsequent period is slower. The maximum concentration of benzyl alcohol is significantly higher for the reaction of DBE in the presence of ZnI_2 than either $ZnCl_2$ or $ZnBr_2$. It is also significant to note that with ZnI_2, no benzyl iodide is formed, and toluene is produced as one of the stable products. The absence of benzyl iodide may be due to the fact that it is rapidly consumed upon formation, since the reactivity of benzyl iodide is known to

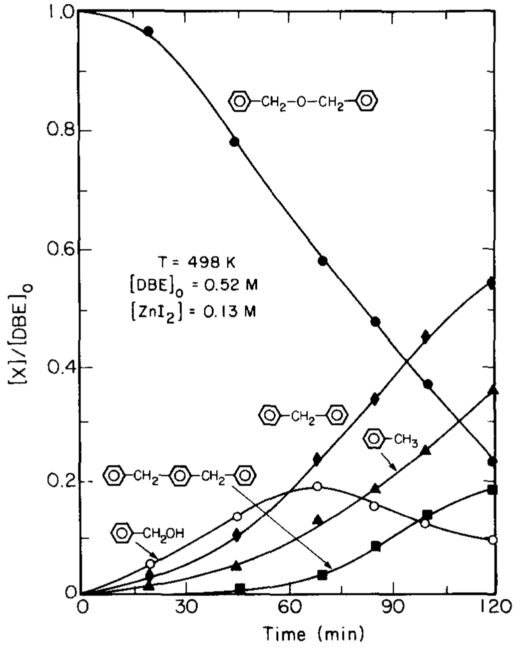

FIG. 3. Concentration versus time profiles for the reaction of DBE in the presence of ZnI_2.

TABLE 1

Product Yields from Reaction of Dibenzyl Ether[a]

Catalyst	P_{H_2} (atm)	Yield (%)			t_{75}[b] (min)
		Diphenylmethane	Dibenzylbenzenes	Toluene	
$ZnCl_2$	20	85	16	0	26
	54	86	16	0	26
	20	83	15	0[c]	26
$ZnBr_2$	19	88	10	1	52
	54	83	16	2	45
ZnI_2	17	73	12	16	110
	48	51	13	25	90

[a] All reactions were carried out at 498 K in benzene using a catalyst loading of 0.13 *M* and an initial DBE concentration of 0.52 *M*.

[b] Time to achieve a 75% conversion of DBE.

[c] 0.52 *M* H_2O added.

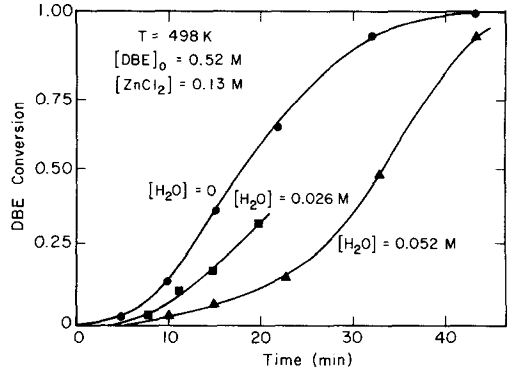

FIG. 4. Effect of water on the reaction of DBE in the presence of $ZnCl_2$.

be much greater than that of benzyl chloride (*8*).

Table 1 compares the product yields for the three catalysts at two hydrogen pressures. In the present context, the yield of a product is defined as the fraction of reacted DBE that appears in that product at 75% conversion of DBE. Also included in Table 1 is the time required for 75% of the original DBE to disappear. It is noted that $ZnCl_2$ and $ZnBr_2$ give similar product yields. ZnI_2 gives lower yields of diphenylmethane and dibenzylbenzenes but produces toluene to compensate. As noted earlier, a small amount of toluene is also formed when $ZnBr_2$ is used as the catalyst. The activities of the three zinc halides decline in the order $ZnCl_2 > ZnBr_2 > ZnI_2$.

Hydrogen pressure has no effect on the yields or the reaction rate using $ZnCl_2$ as the catalyst. A slight increase in reaction rate and a small amount of toluene are found with increasing hydrogen pressure for $ZnBr_2$. With ZnI_2, increasing hydrogen pressure increases the reaction rate and increases the toluene yield at the expense of diphenylmethane. Thus, the sensitivity of the reaction to hydrogen pressure depends on the composition of the catalyst.

Dibenzyl ether was also reacted in *p*-xylene using $ZnCl_2$. The products at 100% conversion were benzylxylene (84% yield) and dibenzylxylenes (15%). The rate of DBE cleavage was nearly identical to that observed using benzene as the solvent.

The influence of water on the cleavage of DBE was investigated by adding small amounts of water to the solvent prior to heating up the solvent–catalyst mixture. Figure 4 shows that the presence of water lengthens the induction period for the onset of rapid reaction of DBE. However, once DBE begins to react rapidly, the rate of reaction is virtually the same whether or not water is present.

Frederick and Bell (*7*) have shown that the addition of HCl to $ZnCl_2$ greatly enhances the activity of $ZnCl_2$ for the cleavage of benzylaryl ethers. The extent to which such promotion influences the cleavage of DBE is shown in Fig. 5. At 466 K, and in the absence of HCl, $ZnCl_2$ shows little activity. As HCl is added, the activity

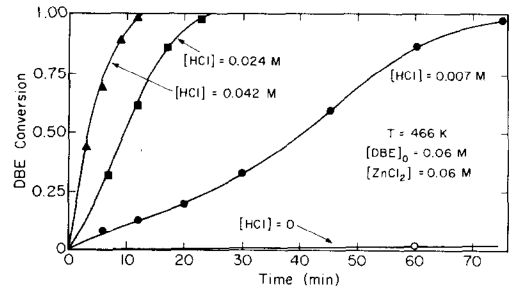

FIG. 5. Effect of HCl on the reaction of DBE in the presence of $ZnCl_2$.

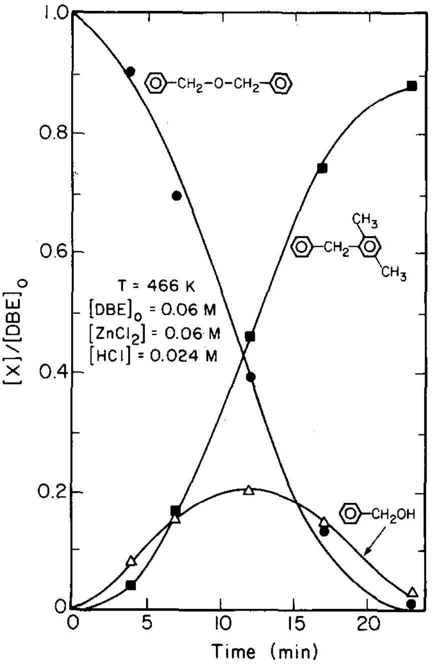

FIG. 6. Concentration versus time profiles for the reaction of DBE in the presence of HCl/$ZnCl_2$.

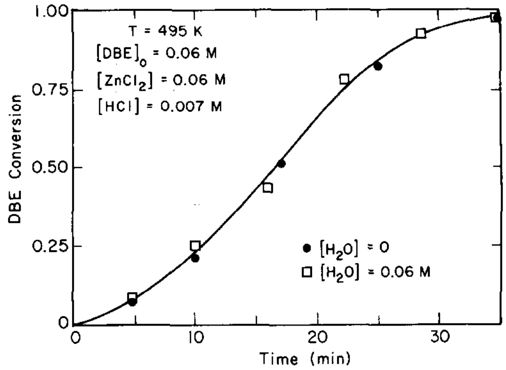

FIG. 7. Effect of water on the reaction of DBE in the presence of $ZnCl_2$.

increases rapidly. Figure 6 shows the concentration versus time curves for a moderate level of HCl addition using *p*-xylene as the solvent. Benzyl alcohol is the only intermediate observed and benzylxylene is the only product at 100% conversion. No dibenzylbenzenes were observed because the initial DBE concentration was one-fourth the level used in the experiment shown in Fig. 1.

In contrast to the $ZnCl_2$-catalyzed reaction, the HCl/$ZnCl_2$-catalyzed reaction was not affected by water addition. Figure 7 compares two experiments with and without H_2O addition using an HCl concentration of 0.007 *M*. The run with 0.060 *M* H_2O gave the same reaction rate and product yields as the run with no water added. This lack of an effect of water was also found for the HCl/$ZnCl_2$-catalyzed reaction of benzylphenyl ethers (*7*).

Benzyl alcohol is formed as an intermediate during the reaction of DBE, regardless of which zinc halide is used. The reaction kinetics of benzyl alcohol were, therefore, studied independently, using $ZnCl_2$ as the catalyst and either benzene or *p*-xylene as the solvent. The rate of alcohol disappearance was found to obey a rate expression that was first order in benzyl alcohol. The apparent first-order rate coefficient is given in Table 2 for several runs using *p*-xylene as the solvent. Similar values of the rate coefficients were obtained for reactions in benzene. The rate coefficient increased rapidly with temperature but was not affected by the initial alcohol concentration. In the absence of added HCl, the reaction followed two parallel paths. Benzyl alcohol either benzylated the solvent or reacted with $ZnCl_2$ to form benzyl chloride. The yield of

TABLE 2

Rate Coefficients and Benzyl Chloride Yields for the Reactions of Benzyl Alcohol[a]

T (K)	Benzyl alcohol concn. (*M*)	*k* (s^{-1})	Benzyl chloride yield (%)
466	0.06	2.2×10^{-4}	[b]
466	0.06[c]	2.5×10^{-2}	100
498	0.06	4.0×10^{-3}	15

[a] All reactions were carried out in *p*-xylene using a $ZnCl_2$ loading of 0.06 *M*.
[b] Could not be determined.
[c] 0.06 *M* HCl added.

benzyl chloride was 15%, and the yield of benzylxylene was 85%.

The reaction of benzyl alcohol in the presence of HCl and $ZnCl_2$ was also examined, since it is well known that alcohols will react with hydrogen halides to form alkyl halides and water (*9*). These experiments were conducted using an HCl concentration of 0.06 *M* and a $ZnCl_2$ concentration of 0.06 *M*. The rate of benzyl alcohol disappearance was much faster than in the absence of HCl and produced benzyl chloride exclusively. This experiment indicates that the reaction between benzyl alcohol and HCl is fast compared to benzylation of the solvent. It is also much faster than the rate of reaction between benzyl alcohol and $ZnCl_2$. Thus, if a significant amount of HCl is present, the benzyl alcohol will rapidly react to benzyl chloride before any other reaction of benzyl alcohol can occur.

Following the rapid conversion of benzyl alcohol to benzyl chloride in the experiments just described, the benzyl chloride slowly reacts with the solvent, xylene, to form benzylxylene. The disappearance of benzyl chloride was observed to follow first-order kinetics and was characterized by $k = 0.001\ s^{-1}$. By contrast, $k = 0.005\ s^{-1}$ when benzyl chloride reacts with xylene in the presence of $ZnCl_2$ but no HCl. The reactions of benzyl iodide in the presence of ZnI_2 and benzyl bromide in the presence of $ZnBr_2$ were also investigated. The rates of both reactions were too fast to measure at 466 K. In contrast to benzyl chloride, both reactions produced toluene in addition to benzylxylene. For benzyl bromide, a 4% yield of toluene was found and for benzyl iodide, a 45% toluene yield was observed. The balance of the benzyl halide in both cases formed benzylxylene.

The present work indicates that benzyl alcohol can react in the presence of $ZnCl_2$ via three paths, as shown in Fig. 8. The first results in the benzylation of the solvent, benzene. The second is the reaction of benzyl alcohol with $ZnCl_2$ to produce benzyl chloride. The third reaction is the rapid reaction of benzyl alcohol with $HCl \cdot ZnCl_2$ to produce benzyl chloride. The second of these processes is the most important to the reaction of DBE because it provides a means for forming HCl from $ZnCl_2$. Once formed, HCl combines with $ZnCl_2$ to produce a more active catalyst than $ZnCl_2$ alone, as shown by the results presented in Fig. 5.

An experiment was performed to test whether the amount of HCl released by the reaction of benzyl alcohol with $ZnCl_2$ would be sufficient to accelerate the reaction of DBE. Benzyl alcohol was reacted in the presence of $ZnCl_2$ using an initial alcohol concentration of 0.24 *M*. This is equivalent to the amount of benzyl alcohol that is produced and reacts during the reaction of 0.24 *M* DBE and, hence, should leave the same amount of HCl on the catalyst. Just after the benzyl alcohol had completely reacted to form benzylxylene, DBE was injected into the autoclave, and the progress of DBE disappearance was followed. The rate of

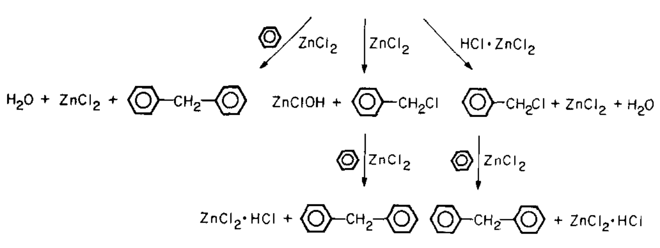

FIG. 8. Reaction paths for benzyl alcohol in the presence of $ZnCl_2$ and $HCl/ZnCl_2$.

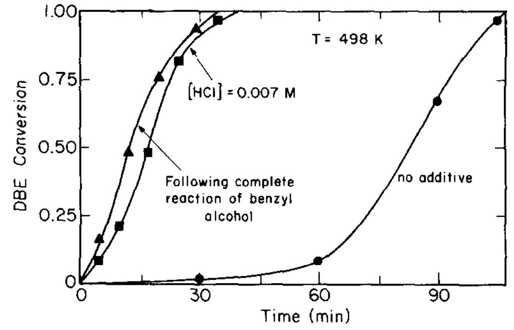

FIG. 9. Effect of previous reaction of benzyl alcohol and HCl on the reaction of DBE.

ether disappearance is shown in Fig. 9, along with the curve for the same reaction without the prereaction of benzyl alcohol. The induction period in DBE conversion disappears if benzyl alcohol is reacted beforehand. The prereaction of benzyl alcohol results in a rate of DBE cleavage that is similar to that observed for HCl addition, as shown in Fig. 9. The reaction with 0.007 *M* HCl is used for comparison because this is roughly the amount of HCl that would be formed from the benzyl alcohol based on the independent reactions of the alcohol. Thus, the production of HCl from benzyl alcohol appears to be sufficient to accelerate the rate of DBE reaction.

DISCUSSION

Reactions of Benzyl Alcohol

Benzyl alcohol is produced as an intermediate during the reaction of DBE. The pathways via which this product is consumed are shown in Fig. 8. If no HCl is present, benzyl alcohol can react with $ZnCl_2$ to form benzyl chloride, which in turn benzylates the solvent. $ZnCl_2$ also promotes the direct alkylation of the solvent by benzyl alcohol. Based on the concentration of benzyl chloride observed during the reaction of benzyl alcohol, and the previously measured reaction rate of benzyl chloride (*9*), it is concluded that roughly 85% of the alcohol reacts to directly alkylate the solvent, and only 15% reacts to form benzyl chloride first. If $HCl \cdot ZnCl_2$ is present, then a rapid conversion of alcohol to benzyl chloride is observed. This reaction is so fast that it will occur to the exclusion of the two reactions catalyzed by $ZnCl_2$.

The rate of reaction of benzyl chloride formed from benzyl alcohol and HCl $ZnCl_2$ was found to be twice as fast as that observed when the benzyl chloride was charged initially. This difference is probably due to the fact that the surface area of the catalyst in the former case is higher than in the latter. As was noted above, the complex formed between $ZnCl_2$ and benzyl alcohol is soluble in the solvent, and the partial dissolution and recrystallization of the catalyst results in an enhancement in the $ZnCl_2$ surface area. From a comparison of the apparent rate coefficients for benzyl chloride for the two cases, it is concluded that the surface area of $ZnCl_2$ is increased by roughly a factor of 2 when the benzyl chloride is produced from benzyl alcohol.

Catalysis by $HCl \cdot ZnCl_2$

The results in Figs. 5 and 6 indicate that once HCl has been generated *in situ* (from benzyl alcohol or benzyl chloride) or added prior to reaction, the rate of reaction of DBE is rapid. A plausible mechanism for this reaction is illustrated in Fig. 10. This scheme is quite similar to that recently proposed by Frederick and Bell (*7*) to explain the reactions of several benzylaryl ethers. The active form of the catalyst is assumed to be the adduct of HCl and $ZnCl_2$, $HCl \cdot ZnCl_2$. In reaction 1, the proton in $HCl \cdot ZnCl_2$ reacts with the oxygen of the ether. The protonated ether then reacts to form benzyl alcohol and benzyl chloride. This step is shown to occur with the intervention of a second unit of $HCl \cdot ZnCl_2$, by analogy with the reaction of benzylphenyl ether (*7*). Benzyl alcohol, produced from the reaction of the protonated ether, can follow the three reaction paths shown in Fig. 8. Since HCl is present, the reaction of the alcohol with $HCl \cdot ZnCl_2$ to form benzyl chloride dominates. In the experiments with HCl ad-

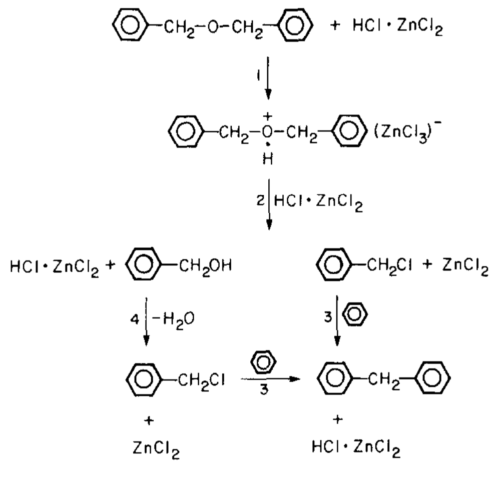

FIG. 10. Mechanism for the reaction of DBE in the presence of HCl · $ZnCl_2$.

dition, only a trace of benzyl alcohol was observed at low HCl levels and no alcohol was found at higher HCl levels. Once formed, the benzyl chloride reacts with the solvent to form benzylated products and regenerates HCl · $ZnCl_2$.

Analysis of the Reaction Kinetics

The mechanism in Fig. 10 was used to represent the kinetics of the reaction of DBE in the presence of HCl · $ZnCl_2$. The autoclave was modeled as a well-stirred, isothermal, batch reactor. Equations (1)–(6) represent the un-steady-state mass balances for the species participating in the overall reaction.

$$\frac{dE}{dt} = -k_1EZ \tag{1}$$

$$\frac{dZ}{dt} = -k_1EZ + k_3C - k_4ZA \tag{2}$$

$$\frac{dI}{dt} = k_1EZ - k_2ZI \tag{3}$$

$$\frac{dA}{dt} = k_2ZI - k_4ZA \tag{4}$$

$$\frac{dC}{dt} = k_2ZI - k_3C + k_4ZA \tag{5}$$

$$\frac{dD}{dt} = k_3C. \tag{6}$$

The symbols in Eqs. (1)–(6) are defined as:

E = concentration of DBE (M),
Z = concentration of HCl · $ZnCl_2$ times the dispersion of $ZnCl_2$ (M),
I = concentration of ether–HCl complex (M),
A = concentration of benzyl alcohol (M)
C = concentration of benzyl chloride (M)
D = concentration of benzylxylene (M).

The concentration of each species is based on the volume of solution. The concentration of HCl · $ZnCl_2$ is multiplied by the $ZnCl_2$ dispersion to account for the fact that only the external surface of the $ZnCl_2$ particles is available for reaction.

The dispersion of the $ZnCl_2$ was assumed to be expressed by the equation

$$d = d_f - (d_f - d_i)E/E_0 \tag{7}$$

where d_i and d_f are the initial and final dispersions of the $ZnCl_2$, and E_0 is the initial concentration of DBE. The rate coefficients for the benzyl chloride reaction suggest that the surface area of the $ZnCl_2$ roughly doubled as benzyl alcohol reacted, and consequently, the value for d_f was chosen as twice the value for d_0 (0.26 m^2/g). Equation (7) assumes that the increase in dispersion is proportional to the fraction of ether that has reacted. This redistribution depends on the conversion of ether, since the reaction of the ether produces benzyl alcohol which, in turn, causes the increase in $ZnCl_2$ surface area. The assumption of a linear relationship between conversion and catalyst dispersion is not justified by any experimental results. It was noted, however, that it was necessary to include some functional dependence of d on E/E_0, in order to achieve a satisfactory representation of the observed concentration versus time profiles. The exact form of the relation connecting d_f to d_0 had only a small effect on the predicted concentration profiles, and hence, a linear form was chosen as a matter of convenience.

The initial conditions for Eqs. (1)–(6), at $t = 0$, are given by

$$\begin{array}{ll} E = E_0 & A = 0 \\ Z = Z_0 & C = 0 \\ I = 0 & D = 0. \end{array}$$

Z_0 represents the initial concentration of $HCl \cdot ZnCl_2$ multiplied by the dispersion of $ZnCl_2$. This assumes that the HCl added to the $ZnCl_2$ is distributed uniformly throughout the $ZnCl_2$. The ratio of HCl to $ZnCl_2$ at the surface is then equal to that ratio in the bulk.

Values for the rate coefficients, k_1, k_2, k_3, were obtained by fitting the experimental concentration versus time curves. The experimental value of the rate coefficient for the benzyl alcohol reaction, k_4, was used. The differential equations were integrated for an assumed set of rate coefficients, using a Runge–Kutta–Gill routine (*10*), and the theoretically generated concentration versus time curves were compared to the experimental curves. If the agreement was poor, a new set of rate coefficients was then chosen to minimize the difference, and the equations were integrated again. A Simplex routine was used to generate the next set of rate coefficients and to minimize the difference between experiment and theory (*11*).

The solid curves in Fig. 5 represent the best fit of the predicted concentration versus time curves to the experimental data for DBE reaction at 466 K. The rate coefficients determined from the simulation of DBE reaction at three different HCl loadings are reported in Table 3. Unique values for k_1, k_2, and k_3 could be obtained because the predicted concentration versus time curves were fairly sensitive to the values of these rate coefficients. The value of each rate coefficient is seen to be roughly independent of the HCl concentration, as would be expected. The mechanism is further supported by the fact that the values determined for k_3 agree very closely with the value of $1.1 \times 10^{-3}\ s^{-1}$ obtained in an independent experiment in which benzyl chloride was reacted with benzene (*7*).

Reaction 2 in Fig. 10 is shown to occur with the intervention of a molecule of $HCl \cdot ZnCl_2$. Attempts were made to model the reaction kinetics for the case in which this species does not participate in reaction 2. It was found that the experimental data for DBE could not be fit in this case.

Catalysis by $ZnCl_2$

The mechanism presented in Fig. 10 does not account for the initial period of slow reaction during which DBE reacts with $ZnCl_2$ (Fig. 1). The behavior of the reaction during this induction period can be explained by the mechanism in Fig. 11. Dibenzyl ether complexes with anhydrous $ZnCl_2$ in reaction 1. If any water is present, it competes for the Lewis acid site, thereby retarding the rate of $ZnCl_2$ with the ether. The $ZnCl_2$–ether complex reacts with an aromatic center to form the benzylated product. Benzyl alcohol can then react by one of the three paths shown in Fig. 8. One of these paths forms benzyl chloride, which in turn produces HCl.

TABLE 3

Rate Coefficients for the Elementary Steps Appearing in the Mechanism Presented in Fig. 10[a]

	0.007 *M* HCl	0.024 *M* HCl	0.042 *M* HCl	Benzylphenyl ether[b] 0.024 *M* HCl
$k_1\ \left(\frac{cm^3}{mole \cdot s}\right)$	8.5×10^6	6.6×10^6	9.2×10^6	4.9×10^6
$k_2\ \left(\frac{cm^3}{mole \cdot s}\right)$	7.8×10^7	6.6×10^7	7.7×10^7	6.0×10^7
$k_3\ (s^{-1})$	1.0×10^{-2}	1.2×10^{-2}	1.1×10^{-2}	4.7×10^{-3}

[a] All values are for 466 K.

[b] These values are taken from Ref. (*7*).

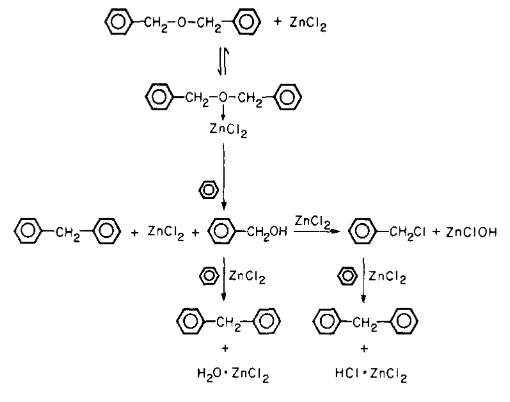

FIG. 11. Mechanism for the reaction of DBE in the presence of $ZnCl_2$.

The mechanism in Fig. 11 can also be used to explain the results obtained with $ZnBr_2$ and ZnI_2. In contrast to $ZnCl_2$, both of these catalysts convert a portion of the DBE to toluene. While the exact mechanism via which toluene is formed is not known, it appears likely that the reaction of the benzyl halide with H_2 in the presence of the catalyst is a key step. This conclusion is based on the observation that benzyl bromide and benzyl iodide react very rapidly to form toluene.

The $ZnCl_2$-catalyzed cleavage of DBE shown in Fig. 1 can be explained in combining the mechanisms presented in Figs. 10 and 11. The conversion of DBE is initially controlled by the reaction sequence depicted in Fig. 11. The benzyl alcohol produced as an intermediate during this phase of the reaction slowly reacts to produce HCl. Once HCl is released, it combines with $ZnCl_2$ to form $HCl \cdot ZnCl_2$. $HCl \cdot ZnCl_2$ is a much more active catalyst than $ZnCl_2$, and its formation results in an acceleration in the reaction rate of DBE. Another result of the production of HCl is the fast rearrangement of benzyl alcohol with HCl to form benzyl chloride. As the reaction proceeds, the conversion of benzyl alcohol to benzyl chloride becomes rapid so that benzyl chloride becomes the predominate intermediate later in the reaction (Fig. 1). The effects of water addition shown in Fig. 4 can also be explained with the aid of the proposed mechanism. The addition of water retards the rate of ether disappearance via the reaction sequence given in Fig. 11 but does not affect the reactions catalyzed by $HCl \cdot ZnCl_2$. It is for this reason that water addition only affects the rate of DBE cleavage during the induction period.

The dependence of catalyst activity on halide composition is different for ZnX_2 and $HX \cdot ZnX_2$. For ZnX_2, the order of activities is $ZnCl_2 > ZnBr_2 > ZnI_2$. This is the order of the ability of ZnX_2 to complex with the oxygen of the ether. The order of activities for $HX \cdot ZnX_2$ is $HI \cdot ZnI_2 > HBr \cdot ZnBr_2 > HCl \cdot ZnCl_2$, as has been found for the reaction of benzylphenyl ether (7), and follows the nucleophilic character of HX.

The cleavage of DBE is very difficult to model mathematically when the two mechanisms are combined. Water is produced during the DBE reaction and contributes a retardation in the rate at which DBE reacts. This process complicates the modeling. The simulation of the $ZnCl_2$-catalyzed reaction was found to be very sensitive to the rate of benzyl alcohol rearrangement to benzyl chloride, and small changes in the rate coefficient for this reaction gave large changes in the predicted concentration versus time profiles. Utilization of the mechanism in Fig. 11 leads to the introduction of several additional rate coefficients. The fits of the theoretically generated concentration versus time curves to the experimental ones was not sensitive enough to the values of these rate coefficients to obtain reliable values.

Comparison of DBE and BPE

A comparison of the reactions of DBE and benzylphenyl ether (BPE) shows both differences and similarities. DBE undergoes cleavage catalyzed by $ZnCl_2$ while BPE does not (*7*). This is consistent with the higher basicity of the oxygen atom in DBE compared to BPE (*12*).

The $HCl \cdot ZnCl_2$-catalyzed reactions of DBE and BPE, on the other hand, are very

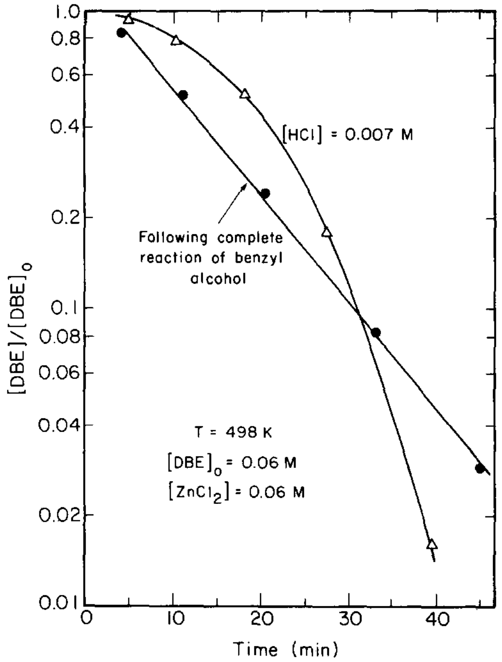

FIG. 12. Plot of log[DBE]/[DBE]$_0$ versus time.

similar. The mechanism proposed for DBE in Fig. 10 closely resembles the mechanism proposed for BPE (*7*). The only difference found between the two reactions is the first-order dependence of the rate of BPE disappearance on the BPE concentration. A plot of the logarithm of BPE concentration versus time is linear, in a manner characteristic of a first-order dependence, on reactant concentration. The plot for DBE is definitely nonlinear, as shown in Fig. 12, for a reaction with 0.007 *M* HCl. The difference between the plots for DBE and BPE is associated with the nature of the products of cleavage, phenol and benzyl alcohol. Phenol is unreactive and does not interact with $ZnCl_2$. Benzyl alcohol, on the other hand, reacts and in addition dissolves and redisperses the catalyst. It is this effect that causes the nonlinearity in the plot of DBE consumption, shown in Fig. 12. The variation in $ZnCl_2$ surface area during DBE reaction can be eliminated, though, if benzyl alcohol is reacted before the reaction of DBE is initiated. The "prereaction" of benzyl alcohol rearranges the $ZnCl_2$ so that the subsequent DBE reaction takes place with a roughly constant surface area. If the data for DBE conversion, after the "prereaction" of benzyl alcohol, are plotted to test for a first-order dependence, a linear relationship is found as shown in Fig. 12. Thus, except for the complications associated with the formation of benzyl alcohol, the $HCl \cdot ZnCl_2$-catalyzed cleavage of DBE follows kinetics similar to those observed with BPE.

Because of similarities in the reaction paths for the two ethers, the rate coefficients for equivalent elementary steps can be compared. Values of the rate coefficients for BPE reaction are presented in Table 3. The rate coefficient for protonation of DBE, k_1, is approximately twice the value for BPE and reflects the greater basicity of the aliphatic ether. The rate coefficient for attack of $HCl \cdot ZnCl_2$ on the protonated ether, k_2, is only slightly larger for DBE. This reaction involves the attack of chlorine on a benzyl group and little effect would be expected from the phenyl or benzyl group at the other end of the ether. The larger value for the rate coefficient for benzyl chloride reaction, k_3, for DBE is due to the increased surface area of $ZnCl_2$ caused by the benzyl alcohol reaction.

CONCLUSIONS

Zinc halide catalysts will promote the cleavage of dibenzyl ether in either their Lewis acid or Brønsted acid forms. In the absence of hydrogen halide, ZnX_2 activates the ether by forming a Lewis acid–base complex with it. Water interferes with the formation of this complex by competing for ZnX_2. In the presence of HX, an adduct is formed, $HX \cdot ZnX_2$, that is catalytically much more active than ZnX_2. The presence of water does not influence the activity of the Brønsted acid form of the catalyst. Activation of dibenzyl ether is achieved by protonation of the ether. The relative activity of the zinc halides depends on which of the two forms is present. If anhydrous

ZnX_2 is the catalyst, the activity decreases in the order $ZnCl_2 > ZnBr_2 > ZnI_2$. On the other hand, if $HX \cdot ZnX_2$ is the prevalent form, the activity decreases in the order $HI \cdot ZnI_2 > HBr \cdot ZnBr_2 > HCl \cdot ZnCl_2$. It is observed that during the reaction of dibenzyl ether in the presence of ZnX_2, a small amount of HX is liberated, which then combines with the zinc halide to form $HX \cdot ZnX_2$. Because the Brønsted acid form of the catalyst is more active than the Lewis acid form, the apparent activity of the catalyst increases after a period of induction during which HX is generated. These observations suggest that the cleavage of ether linkages by $HX \cdot ZnX_2$ could occur during the liquefaction of coal even in absence of intentional addition of HX. Evidence for such a possibility has been cited by Zielke *et al.* (*1, 2*), who have observed that HCl is formed during coal liquefaction in the presence of $ZnCl_2$. The authors proposed that HCl was formed as a consequence of the reaction of $ZnCl_2$ with sulfur.

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