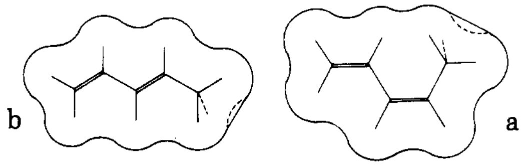

Figure 6. Molecular shape of (a) *cis*-1,3-pentadiene and (b) *trans*-1,3-pentadiene.

certain critical values of the relationship between the form of the included molecules and the form of the channel.

The examination of the polymer structure suggests that the geometric space of the channel maintains its form when the included monomers vary, so that for the monomer with low steric hindrance there is more than one possibility of insertion (at a given thermodynamical stability). In fact, the polymerization of *trans*-1,3-pentadiene yields polymers that are structurally nonhomogeneous and, according to the optical activity values, whose microstructure is not exactly reproducible.

By including *cis*-1,3-pentadiene, a diolefin with a higher steric hindrance, it is possible to obtain a polymer with high structural purity while an increase in the chain isotacticity is obtained. Further confirmation of this trend can be observed in the polymer obtained by inclusion of 2-methypentadiene in DCA.[20]

It is now easy to explain the different behavior of *cis*-pentadiene and *trans*-pentadiene in this inclusion polymerization; Figure 6 shows the differing molecular steric bulkiness of *cis*- and of *trans*-1,3-pentadiene. Clearly, the interactions between *cis*-pentadiene and the channel are greater than between *trans*-pentadiene and the channel; therefore, the steric control of the channel in the *cis*-1,3-pentadiene polymerization is also greater.

The degree of stereospecificity that can be reached with this solid-state DCA polymerization is not noteworthy, particularly if compared with the high stereospecificity obtained with similar systems, such as perhydrotriphenylene and urea. On the other hand, when considering the asymmetric synthesis possible in DCA inclusion compounds, we note that the *trans*-1,4-polypentadiene obtained has the highest optical activity and, which is even more interesting, has a relatively high degree of optical purity. This means that an asymmetric synthesis with a high degree of asymmetric induction occurs in this system.

Registry No. Deoxycholic acid, 83-44-3; *trans*-1,3-pentadiene homopolymer, 25549-62-6; *cis*-1,3-pentadiene homopolymer, 25549-61-5.

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Rate Constants and Activation Energies for Reaction of Benzyl Cation with Ethers in Solution: Initial Step in Carbocationic Polymerization

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ABSTRACT: Rate constants and activation energies for reactions of the benzyl cation with various ethers in solution have been determined by pulse radiolysis. These condensation reactions have activation energies slightly larger (by 0.3–2.0 kcal/mol) than the activation energies calculated for diffusion-limited ion–molecule reactions. Differences in the reactivities of the various ethers with the benzyl cation could be predominantly accounted for by the values of the preexponential factors rather than by the activation energies. Comparison of these rate constants with the relative basicity of the ethers obtained from steady-state systems showed a qualitative agreement.

Introduction

The role of carbocations in the initiation of polymerization reactions has been well established.[1,2] The addition of carbocations to π-, σ-, and n-donor monomers forms the "onium" ion that is the propagating species in polymerization reactions.

Recent interest in oxonium ions is related to the ability of carbocations to initiate the polymerization of cyclic

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ethers, epoxides, and cyclic acetals.[3] The initial reaction between the ether and the carbocation is the establishment of an equilibrium between the carbocation and the tertiary oxonium ion (reaction 1).[4-6] A much slower reaction,

$$C^+ + EH \rightleftarrows (C\text{–}EH)^+ \qquad (1)$$

$$C^+ + EH \rightarrow C\text{–}H + E^+ \qquad (2)$$

which is also significant in some systems, is hydride transfer from the ether to the carbocation to generate a carboxonium ion (reaction 2). Here, C^+ is the carbocation, EH is the ether, $(C\text{–}EH)^+$ is the tertiary oxonium ion, and E^+ is the carboxonium ion.

The initiating step in the polymerization of ethers has been shown to be reaction 1 and/or reaction 2. The triphenylcarbenium ion initiates the polymerization of cyclic acetals and tetrahydrofuran via hydride transfer.[4-6] Here, the initiating step is reaction 2. The tertiary oxonium ion is rapidly formed but does not undergo further reaction with the ether. Recently,[7] the formation of the tertiary oxonium ion has been shown to be the initiating step in the polymerization of tetrahydrofuran in the presence of the diphenylmethylcarbenium ion.

The polymerization of tetrahydrofuran has also been initiated by the reaction of the benzyl cation with the monomer to form the tertiary oxonium ion.[8,9] Here, the carbocation was generated from the reaction of organic halides such as benzyl bromide with selected silver salts. The initiation process, under these circumstances, was slow compared to the reactions of the benzyl cation we have monitored.

The reactivity of various ethers and epoxides toward the benzyl cation and an upper limit for their reactivity toward the trityl cation have been determined in this work. This is an extension of a recent pulse radiolysis investigation in which the initiation step in the polymerization of alkenes in solution was studied and the reactivity of various alkenes toward the benzyl and benzhydryl cation were determined.[10]

The temperature dependence and corresponding Arrhenius parameters of the reaction between the benzyl cation and selected ethers in solution have also been determined in this work. There is qualitative evidence that reaction 1 is reversible, to a minor extent, but it was not possible to determine the magnitude of k_{-1}. There was no evidence that hydride transfer was an important step in the reaction systems studied.

Experimental Section

As previously described[11,12] the source of the electron pulse was a Varian V-7715A electron linear accelerator. The pulse current of 3–4-MeV electrons was approximately 300 mA for 100–800-ns pulses and 600 mA for 40–80-ns pulses. The concentration of the carbocation generated was on the order of 10^{-7}–10^{-6} M.

The "room-temperature" experiments were done at 22 ± 1 °C. The transient absorption was monitored with either the RCA 1P28 or the RCA 7200 photomultiplier. The RCA 7200 was coupled with a Nexus amplifier and had a 10–90% response time of 100 ns. It was used to monitor reactions that had half-lives of more than 1 μs. The RCA 1P28 had a 10–90% rise time of less than 10 ns and was used to monitor reactions with half-lives less than 1 μs. The source of the analyzing light was an Osram high-pressure xenon lamp Type XBO450. It was necessary to flash the xenon lamp to increase the light intensity when the RCA 1P28 detector was being used since no amplifier was being employed. The length of time a system could be monitored with this detector was limited by the time profile of the lamp flash. The maximum duration of a constant level of monitoring light was 40 μs.

The grating monochromator utilized was a Bausch and Lomb Type 33-86-25 *f*/3.4. A double pass of the analyzing light was used to monitor the transients. Standard 20-mm cells with pure silica windows were used as the reaction cell in all experiments.

The temperature work had a similar optical arrangement. The sample cell was suspended in a thermostatic box constructed out of Delrin with double-walled pure silica windows for the analyzing light. The temperature was regulated by heating or cooling with either air or N_2 passed through the Delrin box. It was possible to control the temperature of the sample cell to within 0.1 °C. The temperature range used was −20 to +50 °C for the solvent 1,2-dichloroethane and −50 to +30 °C for the solvent methylene chloride. These limits were imposed by the boiling and freezing point of the solvent and in some cases by the solubility of the compounds being used.

The solvent used in the majority of the experiments was 1,2-dichloroethane. Both methylene chloride and 1,2-dichloroethane were obtained from Aldrich Chemical Co. These were purified by drying with P_2O_5 for several hours and distilled several times in vacuo.

The precursor compound for the benzyl cation was dibenzylmercury (Alfa Ventron Co.). This was purified by recrystallization from pure ethanol. The precursor compounds for the trityl cation were trityl bromide and triphenylcarbinol, both from the Aldrich Chemical Co. These were recrystallized from 1,2-dichloroethane before use.

The ethers used as nucleophiles were diethyl ether (Mallinckrodt, 99%), di-*n*-butyl ether (Matheson Coleman and Bell, 99%), diisopropyl ether (Aldrich, 99%), tetrahydrofuran (Mallinckrodt, 99%), 2-methyltetrahydrofuran (Aldrich, 95%), tetrahydropyran (Aldrich, 95%), propylene oxide (Aldrich, 99%), cyclohexene oxide (Aldrich, 97%), cyclopentene oxide (Aldrich, 98%), and styrene oxide (Aldrich, 97%). All were dried over $LiAlH_4$ or CaH_2 and distilled in vacuo twice before being used.

The phenylcarbenium ions generated were monitored at the maxima of their optical absorption bands. This is 363 nm for the benzyl cation[13] and 434 nm for the trityl cation.[14] The absorption curves of the carbocations were recorded on a Tektronix programmable waveform digitizer, Type 7912AD, and analyzed with a Tektronix 4051 microcomputer.

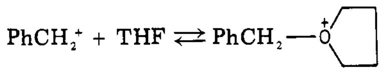
Results and Discussion

Formation and Decay of the Carbocation in the Presence of Ether. Under our experimental conditions, the overall mechanism for the formation and decay of the carbocations in the solvents 1,2-dichloroethane and methylene chloride when ether is present in solution is shown here for reaction of the benzyl cation with tetrahydrofuran (THF):

$$e_{i,s} + DCE \longrightarrow DCE^+ + 2e_s \qquad (3)$$

$$e_{s,th} + DCE \longrightarrow C_2H_4Cl\cdot + Cl^- \qquad (4)$$

$$DCE^+ + (PhCH_2)_2Hg \longrightarrow DCE + PhCH_2^+ + PhCH_2Hg\cdot \qquad (5)$$



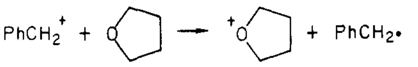
(6)

$$PhCH_2^+ + Cl^- \longrightarrow PhCH_2Cl \qquad (7)$$

e_i is the incident 3-4-MeV electron, e_s is a secondary electron that has less energy than the incident electron, and e_{th} is an electron that is almost thermalized but has not been solvated. The mechanism for the formation of the benzyl cation (reactions 3–5) has been discussed in detail elsewhere.[13a] At high concentrations of the precursor compound (greater than 10^{-2} M) the formation of the benzyl cation was complete within the duration of the electron pulse.

The reaction of the benzyl cation with the ethers proceeds by way of the condensation reaction to form the tertiary oxonium ion (reaction 6). These oxonium ions have been observed in NMR and polarographic studies. Spectroscopic evidence[15] and LCAO calculations[16] indicate that the tertiary oxonium ion does not absorb above 200 nm. The wavelength region below 300 nm is inaccessible in this study because of the strong absorption of the solvents and the solutes used.

There are two reaction pathways other than reaction 6 that could account for the disappearance of the benzyl cation in the presence of ether. These are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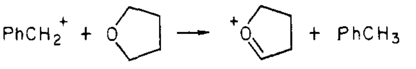
(9)

Reaction 8 is direct charge transfer from the carbocation to the ether, forming the benzyl radical and a radical cation of the ether. This reaction pathway can be eliminated for two reasons: No benzyl radical absorption (317 nm) was observed and the ionization potentials of the ethers (propylene oxide, 10.22 eV; THF, 9.42 eV; diethyl ether, 9.6 eV)[17] are significantly greater than the ionization potential of the benzyl radical (7.76 eV).

Reaction 9 is the hydride-transfer reaction mentioned earlier. Evidence for this reaction was obtained by Penczek[5] for the reaction of the trityl cation with ethers and cyclic acetals in the steady state. The rate constants reported were on the order of 10^{-4} M^{-1} s^{-1} and the ΔH values were approximately 10 kcal/mol. This is compared to rate constants of 10^6–10^8 M^{-1} s^{-1} and activation energies of 3–5 kcal/mol that were determined in this study for the reaction of the benzyl cation with the same ethers. The trityl cation with its three phenyl groups is larger than the benzyl cation. This increase in size should not be expected to account, however, for rate constants that are greater than 10^{10} times as high for reactions between each carbocation and the same ether. The hydride-transfer reaction, if it occurs, would be on a much slower time scale than the reactions monitored in this study.

There is evidence that, when the benzhydryl cation and the trityl cation are the electrophiles, the formation of the tertiary oxonium ion as shown in reaction 6 is reversible. Thermodynamic parameters for the equilibrium between the trityl cation and the various ethers in the solvent methylene chloride have been determined under steady-state conditions.[5] ΔH values for these reactions range from −9 to −17 kcal/mol and ΔS values range from −31 to −60 kcal/(mol K). These values reflect a strong dependence of the equilibrium constant on the temperature of the medium, with the oxonium ion being favored at low temperature.

The reactivities of the diphenylmethyl cation with the same ethers used in this work have been studied but the results have not as yet been published.[18] Interpretations of these results indicate that the reaction mechanism is more complex than the corresponding reaction mechanism for the benzyl cation. It is clear, however, that the tertiary oxonium ion being formed with the diphenylmethyl cation can dissociate to reform the ether and the diphenylmethyl cation.

The absorption spectrum, in the region of λ_{max} for the benzyl cation, is complicated by the presence of an overlapping absorption from an unknown cationic species that has an absorption maximum at 323 nm. This species is generated from dibenzylmercury. The overlap accounts for approximately 18% of the initial optical density observed at the absorption maximum of the benzyl cation (363 nm). The relative amount of this overlap increases with temperature.

The decay of the absorption at 363 nm, when ether was present, characteristically had two kinetic regions. There was a fast initial decay of the absorption followed by a much slower decay. The initial fast portion was atttributed to the addition reaction between the ether and the benzyl cation described in reaction 6. The slow decay was attributed to the decay of the absorption due to the 323-nm species. Spectral data at 50 °C indicated that there was a small amount (less than 5%) of absorption due to the benzyl cation in the slow kinetic region when an alkyl ether or cyclic ether was the nucleophile. This indicated that the oxonium ion formed in reaction 6 was dissociating to a small extent. This dissociation, however, did not significantly affect the magnitude of the rate constants or Arrhenius parameters determined for the condensation reaction.

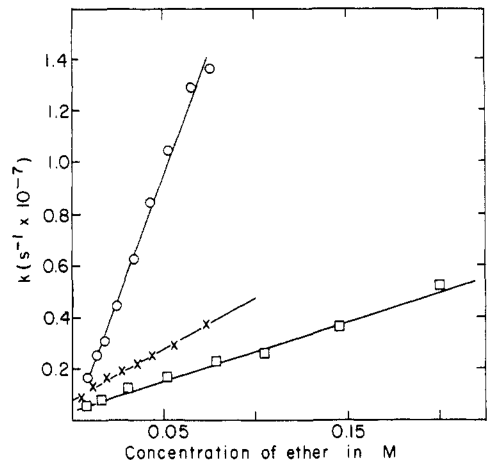

Figure 1. Plot of the pseudo-first-order rate constant against the concentration of diisopropyl ether (□), 2-methyltetrahydrofuran (○), and cyclohexene oxide (×) in the solvent 1,2-dichloroethane at 22 °C.

Reactivity of Ethers toward the Benzyl Cation at 295 K. The following ethers were used as nucleophiles: Alkyl ethers, diethyl ether, diisopropyl ether, and di-*n*-butyl ether; cyclic ethers, tetrahydrofuran, 2-methyltetrahydrofuran, and tetrahydropyran; epoxide ethers, propylene oxide, styrene oxide, cyclohexene oxide, and cyclopentene oxide.

The rate equation for the decay of absorption due to the benzyl cation is

$$-d[PhCH_2^+]/dt = k_6[EH][PhCH_2^+] + k_7[Cl^-][PhCH_2^+] \quad (10)$$

At high concentration of the ether, where [EH] ≫ $[PhCH_2^+]$ and $k_6[EH] \gg k_7[Cl^-]$, eq 10 can be simplified. The second term, which represents the loss of benzyl cation as the result of reaction with the chloride ion, becomes small compared to the first term, and the first term can be rewritten as $k_6'[PhCH_2^+]$, where $k_6' = k_6[EH]$. Equation 10 becomes

$$-d[PhCH_2^+]/dt = k_6'[PhCH_2^+] \quad (11)$$

The reaction of the benzyl cation will be pseudo first order. Integration of eq 11 and conversion from concentration units to optical density units gives

$$\ln [OD_{PhCH_2^+}] = -k_6't + \ln [OD_{PhCH_2^+}]_0 \quad (12)$$

Plotting $\ln [OD_{PhCH_2^+}]$ against time gave a straight line. The slope of this line was k_6'. Plotting these pseudo-first-order rate constants against the concentration gave a straight line with the bimolecular rate constant k_6 as the slope. Typical plots are shown in Figure 1.

The rate constants for the decay of the benzyl cation via reaction 6 at room temperature (22 ± 1 °C) are listed in Table I. These rate constants are well below the diffusion limit for ion–molecule reactions for the solvents used in this study. These rate constants are a direct measure of

Table I
Rate Constants and Arrhenius Parameters for the Reaction of the Benzyl Cation with Ethers in the Solvent 1,2-Dichloroethane[a]

ether	k(295 K), L/(mol-s)	E_a, kcal/mol	A
diethyl ether	1.5×10^7	5.0	8.2×10^{10}
diisopropyl ether	2.5×10^7	4.5	5.8×10^{10}
di-n-butyl ether	1.3×10^7		
tetrahydrofuran	1.4×10^8	3.6	6.5×10^{10}
2-methyltetrahydrofuran	1.8×10^8	4.2	2.5×10^{11}
tetrahydropyran	6.2×10^7		
propylene oxide	1.5×10^7		
cyclopentene oxide	9.1×10^7		
cyclohexene oxide	4.2×10^7	3.1	8.4×10^9
styrene oxide	3.4×10^6	3.2	8×10^8

[a] The error limits are ±15% for the rate constants, ±15% for the energies of activation and ±25% for the preexponential factors.

the reactivity (nucleophilicity) of the ether toward the benzyl cation.

The ability of ethers to complex with positive ions is more frequently related to the "basicity" of the ether. This basicity generally reflects the ability of a compound to complex with a proton (Brønsted base) or the ability of a compound to complex with a cationic center (Lewis base). Relative basicities for the various ethers have been reported by using IR frequency shifts,[19-21] pK_a determinations in sulfuric acid,[22] liquid-phase[23] and gas-phase[23] equilibrium studies, and heat-of-mixing determinations in chloroform.[20] These determinations differ from the rate constants determined in this work in that they represent measurements that were made at equilibrium. There is also much discrepancy concerning the relative basicities of the ethers determined.[19-23] There are, however, a few generalizations that have been made than can be applied qualitatively to the rate constants determined in this work.

A more thorough discussion of the factors affecting the basicity of ethers can be found elsewhere.[24] Generalizations about these factors are as follows: Cyclic ethers are more basic than alkyl ethers, epoxides are less basic than analogous cyclic and alkyl ethers, and the effect of ring size on the basicity of the cyclic ethers is 4- > 5- > 6- ≫ 3-membered rings. In addition to these generalizations there are three effects that determine the relative basicity of the ether in the same solvent. These are inductive effects, which stabilize the "onium" charge center, conjugative effects, which lower the basicity, and steric effects, which interfere with the formation of the oxonium ion. These effects can be clearly seen in the rate constants for the reaction between the benzyl cation and the ethers.

From Table I, the rate constants for the reaction between the benzyl cation and the alkyl ethers are as follows: diisopropyl ether ($k = 2.5 \times 10^7$ M^{-1} s^{-1}), diethyl ether ($k = 1.5 \times 10^7$ M^{-1} s^{-1}), and di-n-butyl ether ($k = 1.3 \times 10^7$ M^{-1} s^{-1}). The rate constants for diethyl and di-n-butyl ether are the same within experimental error. The branched diisopropyl ether was twice as reactive as diethyl ether and di-n-butyl ether. Here, the inductive effect of the branched alkyl group is more significant than the increased steric hindrance.

The rate constants for the reaction of the benzyl cation and the cyclic ethers are as follows: 2-methyltetrahydrofuran ($k = 1.8 \times 10^8$ M^{-1} s^{-1}), tetrahydrofuran ($k = 1.4 \times 10^8$ M^{-1} s^{-1}), and tetrahydropyran ($k = 6.2 \times 10^7$ M^{-1} s^{-1}). These are, in general, more reactive than the alkyl ethers toward the benzyl cation, which is in agreement with the basicity data.[19-23] The 5-membered rings are found to be more reactive than the 6-membered ring. This is again in agreement with basicity data, where the increased basicity of the 5-membered ring has been explained on the basis of favorable steric, ring strain, hybridizational, and conformational aspects.[24,25]

The methyl-substituted tetrahydrofuran is 1.3 times as reactive toward the benzyl cation as the unsubstituted tetrahydrofuran. Here, as in the case of diisopropyl ether, the inductive contribution of the methyl group is more significant than its steric hindrance in determining the reactivity of the nucleophile.

The rate constants for the reaction between the benzyl cation and the epoxide ethers are as follows: cyclopentene oxide ($k = 9.1 \times 10^7$ M^{-1} s^{-1}), cyclohexene oxide ($k = 4.2 \times 10^7$ M^{-1} s^{-1}), propylene oxide ($k = 1.5 \times 10^7$ M^{-1} s^{-1}), and styrene oxide ($k = 3.4 \times 10^6$ M^{-1} s^{-1}). These epoxides show trends that are similar to those observed in the alkyl and cyclic ethers.

The cyclic epoxides such as cyclohexene oxide and cyclopentene oxide are more reactive than the other epoxides. This is analogous to the result obtained in the comparison of the alkyl ethers to the cyclic ethers. The lower reactivity of the epoxides relative to comparable alkyl or cyclic ethers can be explained on the basis of lowered electron density on the oxygen as the result of the large ring strain in the epoxide. Hybridization of the α carbons in the epoxides is sp$^{2.2}$ rather than sp^3 typically observed in unsaturated hydrocarbons.[26] The lower reactivity of styrene oxide is in agreement with the general observation that conjugation lowers the basicity of the ether referred to earlier.

The greater importance of inductive effects rather than steric effects is similar to the results obtained in the determination of the reactivity of various alkenes with the benzyl cation in the solvent 1,2-dichloroethane.[10] Here, the reactivities determined followed the inductive order. The reaction between the benzyl cation and the alkene which gave the most stable product had the highest rate constant. A similar trend has been observed in the condensation reactions between the benzyl cation and the ethers studied in this work.

Reactivity toward the Trityl Cation at 295 K. As previously mentioned, the reactivity of the trityl cation with various ethers has been studied by Penczek and coworkers.[5,6,27] Here, equilibrium constants, their temperature dependence, and the H$^-$-transfer rate constants were reported. In the present work, attempts to determine the rate constant for the formation of the oxonium ion were unsuccessful because the reaction was too slow to monitor in the irradiated systems. The lifetime of the trityl cation in our system is limited by its reactivity with the chloride ion (as in reaction 7 for the benzyl cation). Since no reaction between the ethers and the trityl cation was observed, the upper limit for the forward rate constant can be set at 5×10^5 M^{-1} s^{-1}. This value corresponds to the rate constant needed to obtain a half-life for the condensation reaction that is less than the half-life of the reaction with the chloride ion when the concentration of the chloride ion is as low as possible (3×10^{-7} M) and the ether concentration is as large as possible (usually 0.5 M).

There was a possibility that equilibrium between the oxonium ion and the trityl cation was established rapidly relative to the observed decay of the trityl cation. The observed decay would then represent the reaction of an equilibrium concentration of the trityl cation with the chloride ion. To eliminate this possibility the reaction between tetrahydrofuran and the trityl cation was studied in the solvent methylene chloride at −50 °C. The equilibrium constant at this temperature, as reported by

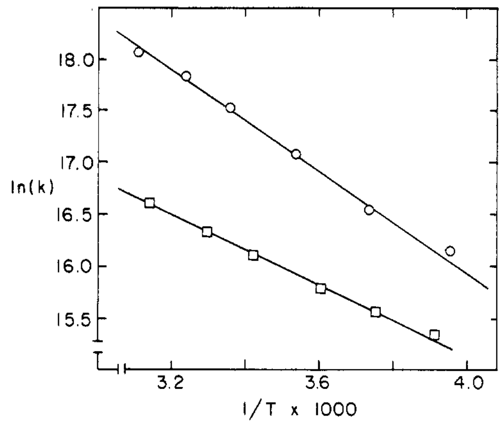

Figure 2. Arrhenius plot for reaction of the benzyl cation with styrene oxide (□) and diisopropyl ether (○) in 1,2-dichloroethane.

Penczek,[27] was 10^4. The rate of the back-reaction would, therefore, be negligible. Under these conditions no reaction of tetrahydrofuran with the trityl cation could be detected. This supports the conclusion that the reaction between the trityl cation and the various ethers have rate constants below 5×10^5 M^{-1} s^{-1}.

Temperature Dependence of the Reaction of the Benzyl Cation with Ethers. The dependence of the rate constant for the reaction between the ethers and the benzyl cation on the temperature was determined for ethyl ether, diisopropyl ether, cyclohexene oxide, styrene oxide, tetrahydrofuran, and 2-methyltetrahydrofuran. Arrhenius plots for these reactions were linear. The linearity indicated that the reaction was proceeding through one mechanism at all the temperatures studied. The energies of activation and preexponential factors determined are listed in Table I. Sample Arrhenius plots are shown in Figure 2.

In the absence of an ether, the benzyl cation reacts with the chloride ion that is formed in reaction 4. This decay is second order with respect to the benzyl cation because the concentration of the chloride ion is approximately equal to the concentration of the benzyl cation. Arrhenius plots for this reaction were linear. The energy of activation determined was 2.9 kcal/mol and the preexponential factor determined was 1.1×10^{13} M^{-1} s^{-1}. The expression for the energy of activation for a diffusion-limited reaction between two oppositely charged ions in a low dielectric solvent is[28]

$$E_a = B + RLT^2$$

Here, B is the slope obtained from a plot of ln (viscosity) vs. $1/T$ multiplied by R, the gas constant, T is the temperature in K, and L (units of K^{-1}) is a constant that gives the dependence of the permittivity on the temperature as $D = D_{\circ C} \exp(-LT)$. B has been determined to be 2.17 kcal/mol and L is approximately 5×10^{-3}. This gives a value of 3.0 kcal/mol for the activation energy, which agrees with the experimental value determined.

The theoretical value for the preexponential factor is on the order of 1×10^{12} M^{-1} s^{-1} in 1,2-dichloroethane.[28] This is a factor of 10 lower than the experimental value determined.

The theoretical value for the activation energy for ion–molecule reactions[28] that are diffusion limited is given by $B + RT$, where B is 2.17 kcal/mol for the solvent 1,2-dichloroethane as previously defined. At 298 K the activation energy for a diffusion-limited reaction is then 2.7 kcal/mol. The energies of activation determined for the reaction between the benzyl cation and the various ethers do not greatly exceed this value. The preexponential factors determined, however, are 10–1250 times lower than the 1×10^{12} value predicted for diffusion-limited reactions. This may indicate that many unreactive collisions between the benzyl cation and the ethers are occurring.

The alkyl ethers ethyl ether and diisopropyl ether have energies of activation of 5.0 and 4.5 kcal/mol for reaction with the benzyl cation. Methyl substitution in the ethers lowers the activation energy and decreases the preexponential factor by a factor of 3.

Methyl substitution in the two cyclic ethers studied increases the preexponential factor and slightly raises the activation energy (they are within experimental error of each other). This was an opposite effect to the one observed for the alkyl ethers.

Styrene oxide and cyclohexene oxide had activation energies of 3.2 and 3.1 kcal/mol. These are within experimental error of each other and are essentially activation energies that show little contribution from an activation barrier in that they are almost within experimental error of the value of 2.7 kcal/mol calculated for diffusion-controlled ion–molecule reactions.

The low reactivity of styrene oxide is not, therefore, determined by an activational barrier but by a preexponential factor that is substantially lower than the preexponential factor for the alkyl and cyclic ethers (60–250 times lower). It is also lower, by a factor of 10, than the preexponential factor for the reaction between the benzyl cation and cyclohexene oxide. This simply reflects the presence of the relatively bulky phenyl group on the carbon α to the carbon–oxygen epoxide linkage in the case of styrene oxide.

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Registry No. Dibenzylmercury, 780-24-5; diethyl ether, 60-29-7; dibutyl ether, 142-96-1; diisopropyl ether, 108-20-3; tetrahydrofuran, 109-99-9; 2-methyltetrahydrofuran, 96-47-9; tetrahydropyran, 142-68-7; propylene oxide, 75-56-9; cyclohexene oxide, 286-20-4; cyclopentene oxide, 285-67-6; styrene oxide, 96-09-3.

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Cationic Copolymers of Isobutylene. 7. Reactivity Ratio Determination by Sequence Distributions Obtained through NMR Analysis

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ABSTRACT: The monomer sequence fractions obtained from the ^1H and ^{13}C NMR spectra of the cationic copolymers of isobutylene (I) with isoprene (IP), *trans*-1,3-pentadiene (tP), and 2,3-dimethylbutadiene (DB) were used for calculating their reactivity ratios. A nonlinear regression analysis utilizing a simplex algorithm and an objective function value permitted the computation of the confidence limits with a defined degree of significance. A comparative test of the first- and second-order Markovian models for the best fit of the experimental data was performed. The reactivity ratios of I–IP copolymer were found to be independent of the degree of conversion, feed composition, and type of catalyst. The values obtained were $r_I = 1.56 \pm 0.19$, $r_{IP} = 0.95 \pm 0.17$; $r_I = 0.59 \pm 0.09$, $r_{tP} = 1.03 \pm 0.19$; and $r_I = 3.20 \pm 1.10$, $r_{DB} = 0.98 \pm 0.53$ (95% confidence limits).

Introduction

In previous papers we studied cationic copolymers of isobutylene (I) with the conjugated diene monomers butadiene (B),[1] isoprene (IP),[2] *trans*-[3] and *cis*-1,3-pentadiene (tP and cP),[4] and 2,3-dimethylbutadiene (DB).[5] This study, which was particularly focused on the structural characterization of the copolymers and their monomer sequence distributions, was carried out mainly by ^{13}C NMR spectroscopy. The structural units present in the copolymers were identified and quantitatively determined by assignment of the signals attributable to the monomer sequences, sometimes up to the level of heptads and octads.[6] Using this structural information, it is possible to determine the reactivity ratios of the monomers by means of a method already applied in the study of epi-sulfide copolymers[7], which is based on a computation program proposed originally by Harwood.[8,9] Recently, this approach has found other applications,[10,11] but the starting point may be considered to be the same, i.e., the association of the relationships of copolymerization statistics with the powerful ability of NMR spectroscopy in polymer characterization for testing mechanistic proposals.[12]

We show in the present paper the results obtained by applying this method in determining the reactivity ratios of I when it is copolymerized with IP, tP, and DB. The collected values are compared with the data reported in the literature and, in some cases, the influence of the experimental conditions (e.g., degree of conversion, feed composition, and type of catalyst) is investigated. Also, the correlation of the experimental data with a first-order or a second-order Markovian model by a simplex algorithm is checked.

The systems I–B and I–cP are not discussed because of their greater complexity and the presence in their spectra of more than one structural diene unit in relatively high concentration.[1,4] The present method has recently been applied to the study of the copolymerization of I with the different isomers of 2,4-hexadiene[13] and 1,1,4,4-tetramethyl-1,3-butadiene.[14]

Experimental Section

Materials. I–IP copolymers were prepared by using, as described previously,[2] a mixture of *n*-pentane/CH_2Cl_2 (1:1 by volume) as solvent at −70 °C and $EtAlCl_2$ as catalyst. Table I shows data for the feed composition, conversion, copolymer composition, and sequence fractions (up to the level of pentads) of ten samples used for studying the reactivity ratios of I and IP. Other samples were obtained under the same conditions but with a solution of $AlCl_3$ in C_2H_5Cl as catalyst. Samples of I–tP and I–DB copolymers employed in these investigations were prepared as described previously.[3,5]

Analyses. ^1H and ^{13}C NMR spectra were obtained and analyzed as reported elsewhere.[1,2] The calculation of the reactivity ratios and their confidence interval was carried out by means of an IBM computer with a program (HAMOCO) written in Fortran language.

Results and Discussion

1. Calculation of the Reactivity Ratios from the Sequence Fractions. The method used in the present paper was described in part previously.[7] The original version[8,9] of the computation program used by us as the basis for our method of calculating the reactivity ratios permits one to obtain (i) the copolymer composition, (ii) the dyad, triad, tetrad, and pentad fractions, and (iii) the sequence number and weight distributions, when the feed composition, conversion, and reactivity ratios are known. The computational procedure can take into account the general form of the first-order Markovian model (terminal

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