Results and Discussion

Such a phase shift makes it difficult to measure J from the coupled spectrum. We report here a simple means for removing this phase shift, so that all lines in the multiplet have identical phase. The modification, called by the palindrome PCJCP (phase corrected J-cross polarization), consists of the conventional JCP sequence[1,5,6] in which either the I or S spin locking rf field remains on an additional time t_{90} given by $\gamma_S B_{1S} t_{90} = \gamma_I B_{1I} t_{90} = \pi/2$. As usual, $\gamma_{I,S}$ is the magnetogyric ratio and $B_{1I,S}$ is the rf field strength for the nuclear species I,S. To the extent that it is instantaneous, the S extension pulse flips the transverse S magnetization into the direction of the static field, where it is unobservable. An I extension pulse, either in phase or in quadrature with the cross-polarization rf, can also be used; the explanation in this case is more involved and will appear elsewhere.[4] The operation of this sequence is shown in Figure 1. During cross polarization the multiplet lines grow at different rates[4] and the conventional multiplet intensity ratios are not preserved either in JCP or PCJCP.

The ease of operation suggests that, for a weak resonance of unknown J, one should use a reasonable guess for the cross-polarization time τ to produce a coupled cross-polarization spectrum by PCJCP. The value of J determined is then used to select an optimal τ for maximum cross-polarization signal.

The PCJCP sequence is best used near resonance ($|\omega_0 - \gamma B_0| \ll \gamma B_1$). Operating significantly off resonance introduces amplitude asymmetries in the S multiplet which the $\pi/2$ extension pulse will convert back into phase shifts. In a reciprocal manner, any phase shifts initially present will, under off-resonance operation, be converted by the pulse extension into an asymmetry in the multiplet.

Acknowledgments. Professor B. C. Gerstein and co-workers kindly provided preprints of their results.

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Liquid–Solid–Liquid Triphase Catalysis. Consideration of the Rate-Limiting Step, Role of Stirring, and Catalyst Efficiency for Simple Nucleophilic Displacement[1]

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Abstract: The kinetics of the triphase catalyzed displacement of chloride ion on n-decyl methanesulfonate employing a series of 1% cross-linked polystyrene resins having pendant tri-n-butylphosphonium groups has been investigated. The rate of displacement (1) exhibited a pseudo-first-order dependency on the mesylate concentration, (2) was directly proportional to the amount of catalyst used, (3) was independent of stirring, (4) was characterized by a free energy of activation of ~30 kcal mol^{-1}, and (5) depended on the catalyst-ion concentration in the resin. In addition, reaction was favored at the external portion of the bead. Taken together, these observations provide strong support that a diffusion-limited chemical reaction is the rate-controlling step. When large quantities of polymer were employed, stirring was needed to increase resin contact with the liquid–liquid interface. Consideration of apparent activation energies, and absorption of n-decyl methanesulfonate in the catalysts, supports the conclusion that inefficient use of ionic sites dispersed throughout the resins is responsible for the low activity observed.

Introduction

The use of solid-phase catalysts to accelerate reaction between substances located in organic and aqueous phases (triphase catalysis, TC) is now well established.[2,3] Based on this technique new and attractive synthetic procedures have become available for nucleophilic substitution, dihalocarbene generation, oxidation, and reduction. Simple nucleophilic displacement has received the greatest attention and, in general, reaction rates under triphase catalytic conditions are lower than those for comparable biphase catalytic processes (e.g., phase-transfer catalysis).[4,5] In order to be able to design more active triphase catalysts, it is essential that the rate-controlling step be identified for each particular system. This has not been done in any of the studies reported thus far.

In principle, the rate-limiting step for TC using polymeric catalysts should be (a) diffusion of reactants across a thin liquid layer surrounding the solid phase (Nernst or film diffusion), (b) chemical reaction at the particle surface, or (c) chemical reaction throughout the polymer matrix. If the rate of chemical reaction is much greater than the diffusion of reactants through the Nernst layer, (a) will control the rate. If chemical reaction is much slower, then the rate would be controlled by either (b) or (c). When diffusion of reactants through the resin (matrix diffusion) is very slow relative to chemical reaction and film diffusion is rapid, chemical reaction taking place at the particle surface controls the rate; if matrix diffusion is fast, chemical reaction occurs uniformly throughout the polymer. Finally, when the rate of matrix diffusion is similar to that of chemical reaction, a diffusion-limited chemical reaction is rate determining.

In the present work we have examined in detail the kinetic features of the triphase catalyzed chloride ion displacement

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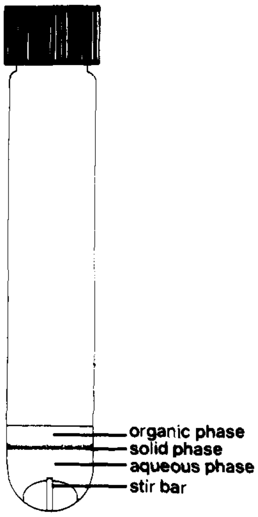


Figure 1. Corning no. 9826 culture tube (25 × 150 mm) containing organic, aqueous, and solid phases plus a Teflon-coated magnetic stirring bar ($\frac{1}{2} \times \frac{5}{16}$ in. octagonal bar with pivot ring).

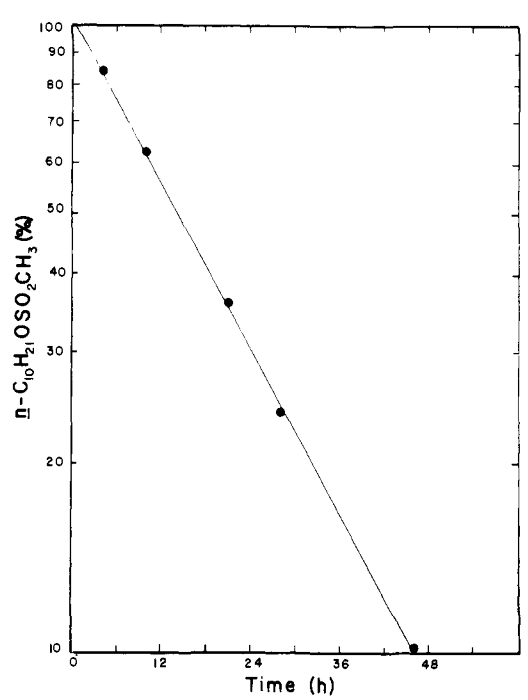


Figure 2. Plot of percent *n*-decyl methanesulfonate in the organic phase as a function of time for the reaction of 3.0 mL of 0.125 M *n*-decyl methanesulfonate in toluene with 10.0 mL of an aqueous saturated sodium chloride solution catalyzed by 0.010 g of **3** at 90 °C carried out as an unstirred process.

on *n*-decyl methanesulfonate (reaction 1) employing a series of related phosphonium-based polystyrene resins **1-4**.[6] Data which we report for this displacement (1) provide strong support for a diffusion-limited reaction as being the rate-controlling step, (2) reveal that a major role of stirring is to increase resin contact with the liquid-liquid interface, and (3) indicate that inefficient use of ionic sites dispersed throughout the resin is responsible for the relatively low activity observed.

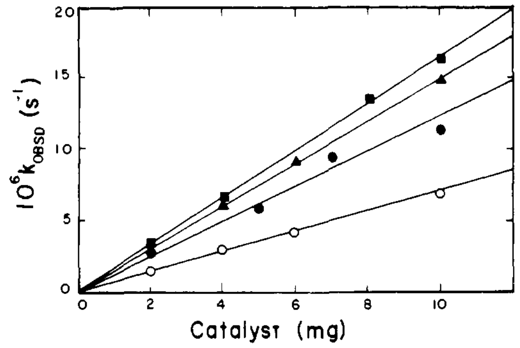
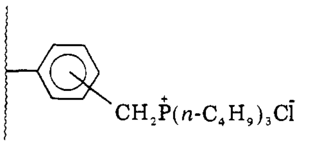


Figure 3. Plot of $10^6 k_{obsd}$ as a function of amount of catalyst **1** (●), **2** (■), **3** (▲), and **4** (○) used for reaction of 3.0 mL of 0.125 M *n*-decyl methanesulfonate (4.0 mL used for reaction with **2**) in toluene with 10.0 mL of an aqueous saturated sodium chloride solution carried out at 90 °C as an unstirred process.

$$n\text{-}C_{10}H_{21}OSO_2CH_3(org) + NaCl(aq) \xrightarrow[\text{catalyst}]{\text{solid phase}} n\text{-}C_{10}H_{21}Cl(org) + CH_3SO_3^-Na^+(aq) \quad (1)$$



functionalized microporous polystyrene-1% divinylbenzene

1, percent ring substitution (prs) = 4; 200-400 mesh
2, prs = 17; 200-400 mesh
3, prs = 52; 200-400 mesh
4, prs = 52; 20-50 mesh

Results

Kinetics of the Displacement. Triphase catalytic systems reported in the literature have been conducted both as stirred and unstirred processes. Since three-phase reactions such as these are intrinsically complex, we have chosen to examine stationary systems for mechanistic work in order to avoid additional complexities associated with the hydrodynamics of stirring.[7] Chloride ion displacement on *n*-decyl methanesulfonate was conducted in 50-mL culture tubes (Figure 1) using procedures described in the Experimental Section. Rates were monitored by following the disappearance of the mesylate from the organic phase. Clean pseudo-first-order kinetics was maintained over at least 3 half-lives and material balance and reproducibility of observed rate constants, k_{obsd}, were good. The only product detected was 1-chlorodecane. Figure 2 illustrates typical kinetic data obtained. For each of the polymers used, pseudo-first-order rate constants were directly proportional to the amount of resin used (Figure 3). For experiments carried out with less than 0.010 g of resin and culture tubes having a toluene-water interfacial area of 4.16 cm^2, *unstirred rates were identical with those of similar reactions in which vigorous stirring was employed.*[8] The complete kinetic equation characterizing these systems can be written in the following form:

$$-d(C_{10}H_{21}OSO_2CH_3)/dt = k_{obsd}(n\text{-}C_{10}H_{21}OSO_2CH_3)^{1.0}$$

where $k_{obsd} = k \times$ weight of resin

For purposes of comparison, we have also examined chloride ion displacement on *n*-decyl methanesulfonate conducted as a phase-transfer catalyzed process, using a soluble phosphonium salt, $C_6H_5CH_2P(n\text{-}C_4H_9)_3Cl$ (**5**).[5,9] Only vigorously stirred reactions were studied and clean pseudo-first-order kinetics was obtained. The distribution coefficients of **5** determined experimentally for the toluene-aqueous sodium chloride system at 80, 90, and 100 °C were $(\mathbf{5})_{org}/(\mathbf{5})_{aq} = 2.13$, 2.47, and 4.0, respectively.

Activation Parameters. Enthalpies and entropies of activation associated with the triphase catalyzed displacements were determined by measuring observed pseudo-first-order rate

Table I. Rate Constants, Activation Parameters, and Catalyst Efficiency[a]

catalyst	temp, °C	10^6k_{obsd}, s^{-1}	10^3k_0,[b] L mol^{-1} s^{-1}	q[c]	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$,[d] eu	$\Delta G^{\ddagger}$ (373.15 K), kcal mol^{-1}
1	80	8.85 ± 0.06	7.20	0.27	11.9 ± 0.5	−48.5 ± 1.9	29.9
	90	14.05 ± 0.72	11.40				
	100	23.11 ± 1.44	18.80				
2	80	12.50 ± 0.09	3.18	0.12	14.9 ± 0.5	−39.2 ± 1.3	29.4
	90	23.75 ± 0.32	6.04				
	100	41.04 ± 2.57	10.40				
3	80	8.19 ± 0.21	1.10	0.04	13.4 ± 1.5	−44.4 ± 5.1	29.9
	90	12.90 ± 0.49	1.74				
	100	24.2 ± 0.97	3.26				
4	80	4.12 ± 0.15	0.56	0.02	13.4 ± 2.4	−45.7 ± 8.2	30.5
	90	6.12 ± 0.23	0.82				
	100	12.18 ± 0.85	1.64				
5	80	75.90 ± 2.3	26.7		9.7 ± 0.2	−50.2 ± 1.0	28.4
	90	120.0 ± 3.1	39.6				
	100	211.0 ± 8.2	58.9				

[a] Reaction of 3.0 mL of 0.125 M *n*-decyl methanesulfonate in toluene with 5.0 mL of an aqueous saturated sodium chloride solution catalyzed by 0.010 g of **1–4** or 0.005 g of **5** carried out as a stirred process. [b] For catalysts **1–4**, $k_0 = k_{obsd} \times$ volume of organic phase/mol of phosphonium groups; for **5**, $k_0 = k_{obsd}/(\mathbf{5})_{org}$. [c] Defined as $k_0^{80\,°C}(TC)/k_0^{80\,°C}(PTC)$. [d] At 90 °C.

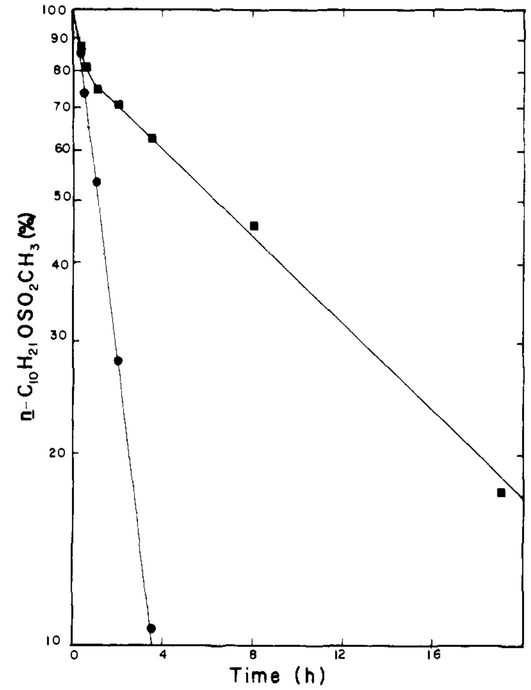


Figure 4. Plot of percent of *n*-decyl methanesulfonate in the organic phase as a function of time for the reaction of 5.0 mL of 0.125 M *n*-decyl methanesulfonate with 5.0 mL of an aqueous saturated sodium chloride solution catalyzed by 0.150 g of **2** at 90 °C carried out as a stirred (●) and unstirred (■) process.

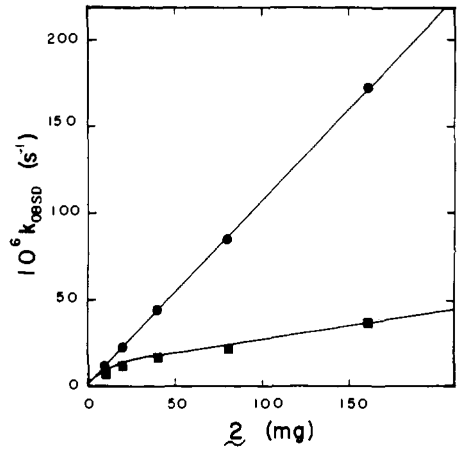


Figure 5. Plot of 10^6k_{obsd} as a function of amount of catalyst **2** used for reaction of 6.0 mL of 0.157 M *n*-decyl methanesulfonate in toluene with 5.0 mL of aqueous saturated sodium chloride solution carried out at 90 °C as a stirred (●) and unstirred (■) reaction. Rate constants plotted for the unstirred reaction were derived from good pseudo-first-order plots obtained after a short induction period of the type shown in Figure 4.

constants at 80, 90, and 100 °C. For **5**, a second-order rate constant, $k_0 = k_{obsd}/(\mathbf{5})_{org}$ was followed as a function of temperature and yielded a good Arrhenius plot. All pertinent data are reported in Table I.

Saturation of the Liquid–Liquid Interface with Catalyst. All of the triphase experiments described above employed a relatively thin layer of resin suspended at the toluene-water interface. When larger quantities of polymer were used, the observed kinetics was characterized by a rapid initial rate followed by a much slower second stage which was pseudo first order with respect to the mesylate (Figure 4). When similar experiments were conducted under vigorously stirred conditions, clean pseudo-first-order kinetics was obeyed throughout the entire reaction and the observed rate was directly proportional to the resin amount (Figure 5). Analysis of **2** recovered from stirred reactions using large quantities of catalyst (e.g., 150 mg) showed that the resin was fully maintained in the chloride form (see Experimental Section).

In contrast, a significant decrease (ca. 33%) in chloride ion content of **2** was noted for a comparable unstirred reaction.

Relative Absorption. Absorption studies described in the Experimental Section indicate that at ambient temperature *n*-decyl methanesulfonate has an identical affinity (within experimental error) with each of catalysts **1–4** under triphase conditions.

Particle Size Effects. Commercial samples of chloromethylated polystyrene from which **2**, **3**, and **4** were derived were prepared by copolymerization of styrene, vinylbenzyl chloride, and divinylbenzene. Since the reactivity ratios of styrene and vinylbenzyl chloride are 0.72 and 1.08, respectively,[11] an approximately random distribution of phosphonium sites must be present throughout these beads. This fact, together with the observation that catalyst **3**, having approximately ten times the surface area of **4** (per gram), exhibited twice the activity found in **4**, shows that reaction is favored at the external portion of the bead.

Discussion

If chemical reaction occurring throughout the polymer were rate limiting in these triphase displacements, the kinetics would be characterized by a rate which is (1) first order with respect to the concentration of *n*-decyl methanesulfonate, (2) directly proportional to the amount of catalyst used, (3) independent of stirring, (4) defined by a significant free energy of activation (>10 kcal mol^{-1}), (5) directly proportional to the catalyst-ion concentration in the resin, and (6) independent of particle size. For a rate-limiting chemical reaction at the bead surface, (1)-(5) would apply and the rate would be inversely proportional to particle size. Film-diffusion control would be indicated by (1) and (2) plus the converse of (3) and (4) and would have an observed rate which is independent of catalyst-ion concentration in the resin and inversely proportional to particle size. Finally, if diffusion-limited chemical reaction were rate controlling, (1)-(4) would apply and the reaction would be favored at the external portion of the bead. In addition, since only chemical reaction and not matrix diffusion is proportional to the concentration of catalytic centers, the observed rate should be dependent on, but not directly proportional to, the ion concentration in the polymer. Taken together, all of the data presented in the Results section are consistent only with a diffusion-limited chemical reaction as being the rate-controlling step.

If we define a parameter α, as the weight of resin used divided by the liquid-liquid interfacial area, the fact that stirring has no significant influence on the observed rate (using low values of α) further indicates that *vigorous stirring does not diminish resin contact with the interface.* For unstirred reactions, as α increased, the amount of polymer located on the organic side only of the liquid-liquid interface increased (visual observation). Much of this additional polymer apparently loses chemical contact with the aqueous phase as evidenced by a substantial depletion in chlorine content of recovered catalyst.

Under such conditions, one would expect to observe an initial stoichiometric biphase plus catalytic triphase displacement which then reduces to the catalytic component. Data presented in Figure 4 confirm that this is, in fact, the case. Vigorous stirring would be expected to increase the liquid-liquid interfacial area, reduce α, and thus increase the effective contact of the resin with the interface. The net result should be (1) maintenance of the resin completely in the chloride form, (2) triphase catalysis as the sole reaction pathway, and (3) participation of all of the polymer beads present in the catalysis. Data presented in Figures 4 and 5 together with chloride ion analysis of **2** recovered from a stirred reaction fully support this view and also demonstrate the need for low α values for effective triphase catalysis.

In order to compare efficiencies of the triphase catalysts **1-4** and the phase-transfer catalyst **5**, a second-order specific rate constant, k_0, was calculated for the former case by dividing k_{obsd} by the ratio of the number of moles of polymer-bound phosphonium groups to the volume of the organic phase. Catalyst efficiencies defined as $q = k_0^{80\ °C}(TC)/k_0^{80\ °C}(PTC)$ are listed in Table I. Since the free energies of activation associated with **1-4** for reaction 1 are the same and since *n*-decyl methanesulfonate has identical affinity toward each of these polymers, the continuous decrease in catalyst efficiency with increasing percent ring substitution must be due to a reduction in the number of active sites which are participating in the catalysis. This conclusion is also consistent with a diffusion-limited chemical reaction. Increased steric congestion throughout the lattice resulting from additional pendant tri-*n*-butylphosphonium groups should decrease the rate of matrix diffusion and help "close off" internal segments of the bead.

From a practical standpoint our results show that optimum triphase catalysis is possible when carried out as an unstirred reaction, provided that a low value of α is employed. This finding is significant since minimal stirring is important in maintaining the physical stability of the catalyst and is particularly attractive for continuous-flow applications. It should have a considerable bearing on the design of future TC reactors. The inefficient use of reactive centers dispersed throughout the polystyrene-based catalysts described here suggests that catalysts having sites located exclusively on the surface of the support should lead to improved efficiency. Studies aimed at evaluating macroreticular and other high surface area polymeric triphase catalysts as well as surface-functionalized microporous polystyrene are now actively being pursued.

Experimental Section

General Methods. Unless stated otherwise, all reagents were obtained commercially and used without further purification. Chloromethylated polystyrene precursors to **2**, **3**, and **4** were purchased from Bio-Rad Laboratories and contained 1.53, 4.08, and 4.08 mmol of chlorine/g, respectively. A chloromethylated precursor to **1** was prepared by chloromethylation of unfunctionalized 1% cross-linked microporous polystyrene (Bio-Rad Laboratories) using established procedures.[12] The resulting resin contained 0.4 mmol of chlorine/g. Triphase catalysts **1-4** were prepared by quaternizing chloromethylated copolymers with tri-*n*-butylphosphine.[4] In all cases, quaternization went to completion.[13] *n*-Decyl methanesulfonate[14] and benzyl tri-*n*-butylphosphonium chloride[15] were prepared using procedures similar to those previously described. Toluene was purified by distillation from sodium benzophenone ketyl under nitrogen. Deionized water was distilled from $KMnO_4/Ba(OH)_2$. The temperature of the oil bath used for kinetic experiments was controlled (±0.5 °C) with the aid of a Therm-O-Watch electronic controller Model L6-1000 (I^2R Co., Cheltenhan, Pa.) attached to a thermometer. All kinetic experiments were conducted in 50-mL culture tubes of the type shown in Figure 1, equipped with a Teflon-lined screw cap. Product mixtures were analyzed by GLC on a Hewlett-Packard Model 5830 A flame ionization instrument (2 ft × 0.125 in. UC-W982 on Chromosorb W column at 160 °C).

Kinetic Methods. Triphase displacement reactions were studied between 80 and 100 °C. In a typical unstirred experiment, 0.010 g of **2** was carefully placed in the bottom of a 50-mL culture tube which was clamped vertically above an oil bath maintained at 90 °C. A saturated aqueous sodium chloride solution (10.0 mL) was slowly added to the tube followed by 3.0 mL of toluene which was 0.0625 M in *n*-hexadecane (internal standard). The tube was then sealed with a screw cap, lowered into the oil bath (maintaining a vertical position), and allowed to equilibrate for 2 h. A sample of *n*-decyl methanesulfonate (92 μL, 0.375 mmol) was then added to the organic layer via syringe and the kinetics monitored by withdrawing 1-μL samples from the organic phase at appropriate time intervals. The disappearance of the reactant was measured by GLC. Kinetic runs were carried out to 30-70% reaction depending upon the experimental temperature. Pseudo-first-order rate constants were calculated with a least-squares program. The reproducibility of the observed rate constants determined at least in duplicate with different stock solutions was good (±10%). Material balance was >95%. Stirring experiments were carried out using procedures similar to the above except that a Teflon-coated stirring bar was added prior to addition of the mesylate.

Partitioning of 5 between Aqueous Sodium Chloride and Toluene. Benzyl tri-*n*-butylphosphonium chloride (0.049 g, 0.153 mmol) was added to a 50-mL culture tube containing 10.0 mL of aqueous saturated sodium chloride solution plus 3.0 mL of toluene. The tube was placed in an oil bath maintained at 80 °C for 15 h and an aliquot (1 mL) was taken from the organic layer and analyzed for chloride ion.[13] Distribution coefficients $(\mathbf{5})_{org}/(\mathbf{5})_{aq}$ determined at 80, 90 and 100 °C were 2.13, 2.47, and 4.00, respectively.

Chloride Ion Content in Recovered 2. Resin **2** was recovered from stirred and unstirred reactions described in Figure 4 (90% displacement) by filtration, washing successively with 3 × 20 mL each of toluene, ethanol, water, ethanol, and dichloromethane, and drying (3 h, 110 °C (0.05 mm)). Chloride ion analysis[13] indicated 1.13 mmol of chlorine/g (96% of original chlorine content) for the stirred and 0.79 mmol of chlorine/g (67% of original chlorine content) for the unstirred reaction.

Relative Absorption. Each of polymers **1–4** (0.10 g) was added to separate 50-ml culture tubes containing 5.0 mL of aqueous saturated sodium chloride plus 5.0 mL of a toluene solution which was 0.125 M in *n*-decyl methanesulfonate and 0.0625 M in *n*-hexadecane (internal standard). After the resulting mixtures were stirred at room temperature for 2 h, 1-μL aliquots were withdrawn from each organic phase and analyzed by GLC. In all cases, the concentration of mesylate was identical with that found in the absence of polymer.

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Structure of 1,2-Difluorocyclopropane and the "Cis Effect"

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Abstract: The geometries of *cis*- and *trans*-1,2-difluorocyclopropane have been obtained by single determinant ab initio geometry optimization at the 4-21 level, using the gradient method in which all internal coordinates are optimized simultaneously. The corresponding 1,2-difluoroethylenes have been reexamined for comparison. Analysis of the geometries and Mulliken population analysis support the explanation given by Bingham for the "cis effect", the general greater stability of the cis isomer of haloethylenes. The same mechanism is shown to interpret the greater stability of the trans isomer of 1,2-difluorocyclopropane. Delocalization is greater in the isomer having the straighter path connecting the substituents and leads to destabilization of that form.

Introduction

Disubstituted ethylenes are generally more stable in the trans than in the cis form, as illustrated by 2-butene, for example. Eyring and co-workers[2] have suggested that a principle of minimum bending of localized and delocalized orbitals plays a major role in determining the fine structure of molecules. Electrons seek the smoothest paths. In quantum mechanical terms, the effect can be interpreted in terms of electron kinetic energy. The principle is, for instance, applied in explaining the so-called "trans effect" in the dissociation of certain metal complexes. For those molecules, the dissociation constants for the trans forms are higher, a fact which is explained by a more favorable pathway in the dissociation of this form. Eyring and co-workers believe that this principle is also responsible for "the usually greater stability of trans over cis disubstituted ethylenes".

There is, however a substantial amount of experimental evidence that, for a number of 1,2-dihaloethylenes, the cis form is more energetically favorable than the trans form. Typically, *cis*-1,2-difluoroethylene is more stable than than the trans form by 1080 ± 120 cal/mol.[3] Even more striking is the difference in electronic energies between *cis*- and *trans*-difluorodiazine, the cis form being in this case more stable by 3050 ± 400 cal/mol.[3]

Several authors have commented on this "cis effect", and it seems clear that one has to take a combination of different effects into account. As pointed out by Craig and co-workers,[3] the F···F distance for *cis*-1,2-difluoroethylene lies on the repulsive side of the van der Waals potential curve, and Binkley and Pople[4] estimate the Coulomb repulsion to be 1.2 kcal/mol lower in *trans*-1,2-diethylene than in the cis form, suggesting that the extra stabilization of the cis form must amount to about 2 kcal/mol.

There are two fundamentally different sources to the possible factors leading to this so-called "cis effect". One is the various factors leading to an extra stabilization of the cis form, the other the possible sources leading to a destabilization of the trans form. We will list the possible sources and refer to previous articles in the field for a more extended discussion.

Three different types of attractive forces have been proposed: contribution of resonance structures, a pπ attraction, and a pσ attraction. The first has been proposed by Pitzer and Hollenberg[5] and is based on contributions of resonance structures of the kind X^-;CHCH=X^+. This type of structure would lead to a net attraction between the halogens and should cause a relatively long C-C bond. The other cis stabilizing effects are based upon overlap between fluorine–fluorine lone pairs. Hoffmann and Olofson[6] have rationalized the stability of *s*-

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