indicate that the cis conformer contains more than one molecule per unit cell.

The infrared and Raman spectra of cyclopropyl isocyanate have been investigated in detail. The band contours for the two conformers calculated from the experimental rotational constants do not differ significantly. Furthermore, since most structural parameters in the trans and the cis forms are found to be similar, their vibrational spectra of the fluid phases are also expected to be similar, resulting in a severe overlap of bands. Therefore, it is very difficult to find convincing evidence for the presence of more than one conformer in the vibrational spectra without the help of high-resolution infrared spectra of the gas. A similar situation was found for cyclopropyl isothiocyanate where the vibrational analysis[19] preceded the microwave study,[3] and it could justify the presence of only the cis conformer, whereas the microwave data clearly proved that both the cis and trans forms exist in the gas phase. Subsequently, from the electron diffraction results[4] it was found that the trans form is 72% abundant at 35 °C temperature in the gas phase. In the present study a complete vibrational assignment has been proposed for the normal modes of cyclopropyl isocyanate, and conformer bands have been assigned for several of these modes.

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Supplementary Material Available: Tables of rotational and vibrational frequencies and their assignments (7 pages). Ordering information is given on any current masthead page.

The Continuously Rotated Cellular Reactor

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Abstract: Cells are created in liquids in the annular gap between concentric cylinders when the inner cylinder is rotated—the Taylor vortex. The continuously rotated cellular reactor, CRCR, is the development of this phenomenon into a practical reactor with reaction localized in individual cells. The reaction locus is selectable by reactant concentration and stoichiometry. Reaction time is inversely proportional to the cylinder rotation frequency. A column of cells with discrete pH values is developed by the neutralization of HCl with NaOH in 2 h. A robust pH column is prepared with phosphate buffer solutions. Molecular transport in the CRCR is given by the Gaussian equation $\langle \bar{n} - {}^1/_2 \rangle = 4\pi DFt/d^2F_c$, where $\bar{n}$ is the mean cell number, d (cm) the gap radius, F (Hz) the inner cylinder and F_c the critical Taylor frequency, t (s) the time, and D (cm^2/s) the molecular diffusion constant. Potential applications are mentioned.

A simple apparatus is introduced which provides spatial and temporal control of solution reactions and the potential for molecular selectivity. The continuously rotated cellular reactor (CRCR) is the equivalent of the continuously stirred tank reactor[1] but is generated in a *single* vessel. The CRCR depends on the phenomenon of the Taylor vortex.[2,3]

The Taylor vortex is generated in a liquid in the annular gap ($d = b - a$ cm) between a rotating (F Hz) inner cylinder (o.d. $= 2a$ cm) and a stationary outer cylinder (i.d. $= 2b$ cm). The vortex motion creates cells of uniform height ($\sim d$ cm),[3,4] in which the fluid spirals helically as it rotates about the inner cylinder. The vortices are counterrotating in adjacent cells, and the angular momentum in the vertical plane changes sign at the cell boundaries (Figure 1).[5] The boundaries are sharp and horizontal provided $F_c < F < \sim 10F_c$, where F_c is the critical frequency for onset of the Taylor vortex.[3,6] Uniform rotation maintains the basic cellular form and motion indefinitely. Each cell contains a central core whose rotation is unperturbed by the surrounding liquid.[5,7] The phenomena of stable liquid cells containing unmixed cores led us to explore the practical potential of a reactor based on vortex motion.

A CRCR was constructed from a 100-mL graduated cylinder, a 1-cm Truebore stirrer centrally located with ground glass joints, and an overhead stirrer operating at 0.5–3 Hz. For water in the CRCR, F_c was calculated (see Experimental Section) to be 0.247 Hz. Samples were added and removed by syringe through a sidearm. The operation of the CRCR is illustrated by the generation of a column of pH cells from HCl, NaOH, and indicator (Figure 2). A more robust pH column can be generated rapidly by combining solutions of H_3PO_4, Na_3PO_4, and pH 7 phosphate buffer at 1 Hz for 10 min and the pH profile maintained for 5–10 h at 0.5 Hz (Figure 3).

Key qualitative features are the following: (1) Sharp cell boundaries can be maintained for hours between reactive solutions differing in concentration by 10 orders of magnitude. (2) Reaction is localized to the cells immediately adjacent to the reaction interface. (3) The location of the reaction interface is established rapidly (<5 min) and is selected by concentration, stoichiometry, and diffusion constant. For equimolar acid/base solutions, the interface occurs at the column center. (4) Reaction time is inversely proportional to F and so may be selected. (5) Reagents can be added to or removed from any point in the column by syringe while maintaining the cellular structure. (6) Density differentials can be tolerated as shown in Figure 2 where the denser base solution is located between the less dense acid layers. When the stirrer is stopped, the base layer flows to the bottom of the

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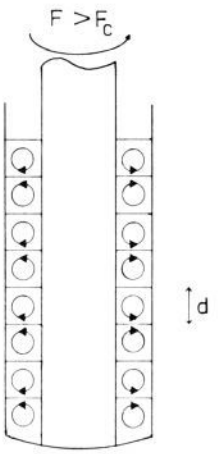

Figure 1. Pictorial representation of Taylor vortex cell motion. The major flow is in the same sense as the inner cylinder. The vortices spiral about this azimuthal flow as shown.

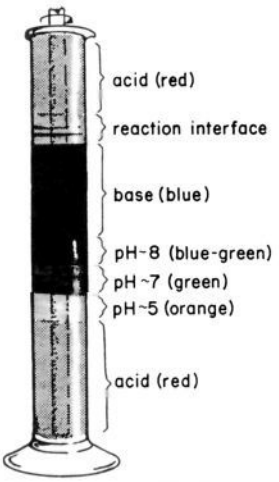

Figure 2. The CRCR showing the development of a pH column from HCl (2.5 mM) and NaOH (2.5 mM) after 2 h. Universal indicator was used for visualization. See Experimental Section for details.

cylinder within 2 min. (7) Temperature differentials can also be tolerated as the vortex motion overrides localized convective processes.

The spatial localization of reaction can be observed visually in the luminol reaction.[8] Light emission is localized in the cells adjacent to the reaction boundary which is selected by reagent and concentration. The cellular structure is maintained despite the continuous evolution of oxygen.

In a quantitative study we have shown that molecular transport occurs by driven and random Gaussian diffusion.[9] The transport equation is

$$\langle \bar{n} - \tfrac{1}{2} \rangle = 4\pi DFt/d^2F_c \qquad (1)$$

where $\langle \bar{n} \rangle$ is the mean number of cells traveled in t, by a species with diffusion constant D cm^2/s. This equation applies when the cell concentrations have been radially equilibrated as will generally be true for the CRCR. It was established through dye tracer studies monitoring cells 3, 4, and 5 from an equilibrated source cell. Intercell transport is initiated at the cell periphery and radial equilibration is slow.[10] When radial equilibration is incomplete, e.g., for dye transport into a long liquid column, the concentration

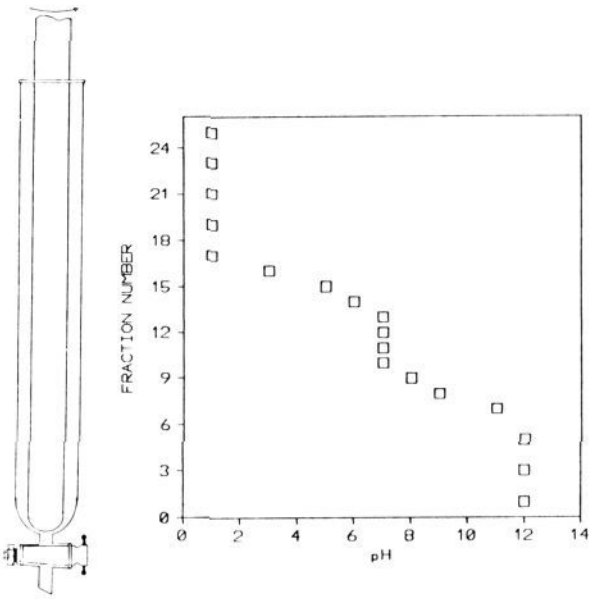

Figure 3. A practical pH column formed in a CRCR with phosphate solutions (see Experimental Section). The pH distribution (4-mL fractions) was formed by rotation at 1 Hz for 3 h.

versus cell number again follows a Gaussian distribution at a fixed development time. The inflection point defined in eq 1 must then be modified to eq 2 to approximate the effects of radial equilibration. It has been verified experimentally[9] that the two

$$\langle \bar{n} - \tfrac{1}{2} \rangle = \pi F\sqrt{2Dt}\,/\,F_c d \qquad (2)$$

equations become equivalent when the development time for peripheral dye transport in a column is $d^2/8D$. However, for the fast reactions employed in the CRCR studies to date, intracell equilibration is relatively rapid and eq 1 applies.

The Taylor vortex is robust in that, provided gap ratios in the vicinity of 0.5 are used, F_c is almost independent of geometric artifacts.[4,11] Stable cells may be generated in square[4b] or conical[11] vessels. Reaction vessels can be scaled up (eq 1–3). Reactors from milliliter to liter scale have been operated effectively. Density differences affect the time but not the form of the development. A column with 0.1 M NaOH (0.995 g/cm^3) above 0.1 M HCl (0.991 g/cm^3) develops three times more rapidly than one with HCl above NaOH. We have noted that neutralization occurs more rapidly at the outward flowing—faster moving[7,12]—cell boundary.

Higher rotation frequencies especially with gap ratios closer to 1.0 lead to more complex boundaries, but the cellular character is maintained.[3,13] Recently Tam and Swinney[14] have measured dye transport as a function of rotation frequency and gap size under these turbulent flow conditions. Equation 2 provides an order of magnitude estimate of their measured values. Thus the CRCR is predicted to be operational at substantially higher frequencies than we have studied.

The CRCR is a novel reactor. It provides control of the time and spatial location of reactions in liquids (eq 1). The location of a reaction is selectable from the column geometry and the concentration and stoichiometry of reaction. The reaction time can be chosen, within the limits set by fast mixing (e.g., stopped flow) and pure diffusion, as molecular transport is directly proportional to the cylinder rotation frequency F. The possibility for molecular selectivity through differences in diffusion constants

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also exists. Potential applications of the CRCR include the following: (1) synthesis, where controlled addition and/or high dilution is critical; (2) mechanism, steady state generation of reactive intermediates in defined locations, e.g., for spectroscopy; (3) analysis, separations based on pH, diffusion, or other field flow fractionation techniques;[15] (4) surface and thin film reactions through the use of immiscible liquids;[16] and (5) oscillating reactions.[17]

Experimental Section

A CRCR was constructed from a 100-mL graduated cylinder fitted with a female ground glass joint and a sidearm for injection and removal of samples. The inner cylinder was a 1-cm Truebore stirring rod that was centrally positioned with a stirring guide fitted with a male joint. For water in the CRCR, F_c was calculated to be 0.247 Hz. The critical frequency is estimated from eq 3[3,5,6] by using the parameters $a = 0.50$ cm, $b = 1.29$ cm, $q = a/b = 0.39$, $T_c(q) = 8305$, and $\nu(H_2O) = 8.93 \times 10^{-3}$ cm^2/s, where ν is the kinematic viscosity of the solvent and T_c is the Taylor number.[6] Rotation was provided by an overhead stirrer over the range 0.5–3 Hz.

$$2\pi F_c = (\nu/ad)[T_c(a + b)/4d]^{1/2} \quad (3)$$

The pH Column (Figure 2). The column was prepared by addition of HCl (28.0 mL, 2.50 mM) followed by water (8.0 mL) and then NaOH (28.0 mL, 2.50 mM). Addition was performed by syringe with the tip bent horizontally. The inner rod was rotating at 2 Hz. After 2 h, a second addition of HCl (20 mL) was made to the top of the column to show the sharp cell boundary and the tolerance for density differences. Figure 2 is an artist's rendition of a photograph taken after the second HCl addition. Fisher Universal Indicator (5%) was present in acid and base solutions for visualization. Preferential reaction at the outward flow boundary generates major pH discontinuities every second cell.

A Practical pH Column: pH Gradient Development Apparatus. The pH gradient in Figure 3 was developed in a CRCR constructed from a 250-mL Kimax buret (i.d. 3.12 cm) and glass tubing (o.d. 2.20 cm). The glass tubing terminated with a precision blown female ground glass joint that was placed over a #2 rubber stopper. The rubber stopper had a hole drilled through it and was placed over the shaft of a laboratory stirrer motor. The motor was connected to a variable transformer which allowed adjustments of the rotation frequency. With the inner glass tube resting in the rounded bottom of the buret, and the motor carefully positioned above the buret, the tube rotated with minimum wobble. The critical frequency for Taylor vortex onset for this setup with water as the fluid ($\nu = 8.93 \times 10^{-3}$ cm^2/s) is calculated as 0.224 Hz, using eq 3 above.

pH Gradient Development Technique. The pH gradient was developed with use of 0.15 M H_3PO_4, 0.156 M Na_3PO_4, and pH 7 buffer solution prepared from 9.1 g of KH_2PO_4 and 18.9 g of Na_2HPO_4 (anhydrous) per liter of solution.

Na_3PO_4 (35 mL) was placed in the bottom of the column. With the inner tube rotating at about 1 Hz, 30 mL of the pH 7 buffer solution was carefully injected on top of the Na_3PO_4. This was done with a 50-mL syringe and 20-gauge needle. During the injection, the stream of solution was directed at the inner cylinder to help reduce convective mixing caused by the downward flow. H_3PO_4 (35 mL) was then injected onto the column with the same care as the previous addition.

With the rotation at 1 Hz the column quickly (5 min) develops (visualized with Fisher Universal indicator) into 5 distinct pH regions (pH's: <4, 5–6, 7, 8–9, >10). If the rotation is kept at 1 Hz the column will completely neutralize in about 5 h. If the rotation frequency is reduced to below 0.5 Hz, the column requires 10–15 h for neutralization.

The pH gradient shown in Figure 3 was developed without Universal indicator. After 3 h of development at 1 Hz, the column was drained through the buret's stopcock and 4-mL fractions were collected. The draining of the column was done with the inner cylinder rotating at about 0.5 Hz and at a drain rate of 4 mL/min. The fractions were analyzed with Hydrion pH paper.

Luminol Oxidation. This reaction was run in the 100-mL graduated cylinder CRCR. The luminol–copper II complex[8] (35 mL) was placed in the bottom of the reactor. With the stirrer rotating at 1.2 Hz, water (30 mL) was carefully injected on top of this solution. Finally a 1% H_2O_2 solution (10 mL) was injected to the top of the liquid column. After the addition of the H_2O_2, a bright band of chemiluminescence is detectable at the midpoint of the column. The band of light, which is approximately 1–2 cells wide, slowly moves down the column as the reaction proceeds. The process lasts approximately 30 min. In other runs, reaction time was found to decrease as the excess peroxide concentration increased. Vigorous oxygen evolution occurs throughout the reaction.

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