Systematic design of chemical oscillators. 17. Birhythmicity and compound oscillation in coupled chemical oscillators: chlorite-bromate-iodide system

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octane at 120 °C was analyzed in the early reaction stages (less phosphites was found to be very rapid as was originally reported by Wawersik and can be no more than 5%.

The mass spectrometric analysis of the isocyanide reactions are about one-hundredth those for CO or (13CO). The half-life of the fast reaction of the Mn2(CO)10 isocyanide reactions is 37 kcal/mol (eq 1); kinetic analyses of the Mn and Re isocyanide reactions were in progress.

Acknowledgment. This research was supported by the National Science Foundation. N.J.C. thanks the CSIR and the University of the Witwatersrand for financial support while on sabatical leave. We especially thank Sherri Ogden and Leah Zebre of the UCB Mass Spectrometric Facility for assistance in the mass spectrometric analyses.

Registry No. Mn2(CO)10, 10170-69-1; P(C6H5)3, 603-35-0; (CH3)3C-C0, 7188-38-7.

Supplementary Material Available: Experimental procedure and Figures 1–4 for observed mass spectrometric data in the 13CO-Mn2(CO)10 reaction, the (CH3)3CNC reaction with M2(CO)10 and Mn(13CO)10, the (CH3)3CNC reaction with Mn2(CO)10 and Mn(13CO)10, catalyzed by Pd on charcoal, and the (CH3)2PC reaction with Mn2(CO)10 and Mn(13CO)10 (7 pages). Ordering information is given on any current masthead page.

Birhythmicity and Compound Oscillation in Coupled Chemical Oscillators: Chlorite–Bromate–Iodide System

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The recent success of systematic approaches to the design of chemical oscillators has been accompanied by increased interest in more complex dynamical phenomena such as chemical chaos. Just as the first deliberately designed chemical oscillator was constructed by coupling two bistable systems, one may ask what phenomena might arise if two oscillatory reactions were linked through a common species.

Heilwell et al. and Cooke have investigated the Belousov–


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Zhabotinsky (BZ) and Briggs–Rauscher systems, respectively, with two or more independently oscillatory organic substrates present. Both of these studies, which were done under batch (closed system) conditions, showed the surprising sequence of oscillations characteristic of one substrate followed by a quiescent period followed by a further series of oscillations characteristic of a second substrate. Maselkó has studied the bifurcation behavior of a mixed substrate BZ system in a stirred-flow reactor (CSTR).

In perhaps the most thorough theoretical investigation of the phenomena that may arise from the coupling of chemical oscillators, Decroly and Goldbeter considered a flow system containing two allosteric enzymes for which the product of one constitutes the substrate of the other. In addition to regimes in which only a single stationary or oscillatory state is stable, they found smaller range the frequency is very close to that of the pure A state and that the frequency increases as the A state decreases, like the A state but unlike the B state. It thus appears that the B oscillator is entrained by the lower frequency, higher amplitude A oscillator.

In agreement with the calculation of Decroly and Goldbeter, the compound oscillation is illustrated in Figure 2. At high flow rate, we have the A state, and at low flow rate the B state. In an intermediate range these states merge into a single complex oscillation. Note that at the upper end of the compound oscillation range the frequency is very close to that of the pure A oscillator and that the frequency increases as k₀ decreases, like the A state but unlike the B state. It thus appears that the B oscillator is entrained by the lower frequency, higher amplitude A oscillator.

In Figure 3, we show a section of the phase diagram in the flow rate–iodide plane. In addition to the two simple and one compound oscillating states, there exist three different stable stationary states. In agreement with the calculation of Decroly and Goldbeter, the regions of birhythmicity and complex oscillation are found to be relatively small.

On comparison of the present results with those obtained for the component subsystems, it is tempting to identify the oscillatory states A and B with those of CIO₃⁻–I⁻ and BrO₃⁻–I⁻, respectively. This identification is based upon similarities in waveform, amplitude, period, and absolute potential. A true understanding of the full system, however, must await the development of mechanisms for the component oscillators and a more thorough experimental study.

Whether the observations reported here will be of use in understanding the proposed role of coupled oscillators and birhythmicity in biochemical regulation remains to be seen. Our results do support the notion that the variety of chemical oscillators is now sufficient that almost any phenomenon predicted from the study of nonlinear differential equations may be realized in an appropriately designed chemical system.

Acknowledgment. We thank Jerzy Maselko, György Bazsa, Robert Olsen, and Kenneth Kustin for helpful discussions. This

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**Figure 1.** Birhythmicity in the chlorite–bromate–iodide system. Potential oscillation, input concentrations, and flow rate. At the same values of temperature, input concentrations, and flow rate, the system can exist in either a low-potential, high-amplitude oscillatory state (A) or a high-potential, low-amplitude oscillatory state (B). Transitions between the states can be induced not only by changes in the flow rate but also by sufficiently large one-time perturbations with oxidants (e.g., bromate, chloride, permanganate) to generate a single oscillator with a complex waveform.

**Figure 2.** Compound oscillation (C) between A and B states as flow rate is changed. Fixed constraints as in Figure 1, except [I⁻]₀ = 4.0 × 10⁻⁴ M.

**Figure 3.** Phase diagram in the k₀=[I⁻]₀ plane (fixed constraints as in Figure 1): O, oscillatory state A; ◊, oscillatory state B; ●, compound oscillation C; ○, birhythmicity, A and B both stable; □, high-potential stationary state; ▲, low-potential stationary state; ◇, intermediate-potential steady state. Combinations of two symbols imply bistability between the corresponding states.

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First and Second Acidity Constants for Some Indenyl and Fluorenyl Hydrocarbons: Coulombic Effects in Ion Triplets

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We recently reported that the first and second ion pair pK's in the cesium cyclohexylamide (CsCHA)-cyclohexylamine (CHA) system for 9,10-dihydroanthracene differ by only 3.8 pK units.2 Where the spectra overlap seriously, we use the experimental pKACsCHA values are summarized in Table 1.

Table 1. Absorbance (nm) and pKACsCHA Values

<table>
<thead>
<tr>
<th>RH</th>
<th>R'C+</th>
<th>R'2C++</th>
<th>pKACsCHA</th>
<th>pK2CCHA</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>345 (26.1)</td>
<td>372 (32.0)</td>
<td>19.81a</td>
<td>20.27a</td>
</tr>
<tr>
<td>2</td>
<td>408 (6.2)</td>
<td>413 (16.0)</td>
<td>20.51b</td>
<td>20.65b</td>
</tr>
<tr>
<td>3</td>
<td>321 (41.0)</td>
<td>343 (28.0)</td>
<td>22.26a</td>
<td>25.67a</td>
</tr>
<tr>
<td>4</td>
<td>370 (12.0)</td>
<td>355 (82.0)</td>
<td>22.24a</td>
<td>27.30a</td>
</tr>
</tbody>
</table>

a ±0.2. b ±0.3.

Figure 1. Ion triplet structure of dialkali cation salts of 9,9'-bifluorenyl (2).

Figure 2. Coulomb interactions for a point charge model of a dicarbanion.

Figure 3. Ion triplet structure assumed for 4c.

pK's of the indenofluorenes are slightly lower than for fluorene, as one might expect for phenyl-substituted fluorenes. The pK2CCHA values, however, are most unusual; ΔpK is 0.5 for 1 and only 0.14 for 2. The pK's for 3 and 4 are greater, 3.4 and 5.1, respectively, and differ substantially from each other despite their similarity in structure.

The X-ray crystal structure of a dilithium salt of 2 has been reported; in this structure the two fluorenyl ring planes are twisted with respect to each other, and solvated Li⁺ groups are placed above and below the central C-C bond (Figure 1). A similar structure is plausible for the dicesium salt and for the dicesium salt of a dicarbanion.

Consider the collection of point charges shown in Figure 2. For such a system the following equation holds for the electrostatic energy, Eel:

\[ E_{el} = \frac{1}{R_{-}} + \frac{1}{R_{-} + 4/R_{-}} \]

where \( R_{-} \) is the distance between positive and negative charges. It is readily shown that \( E_{el} \) is negative in the \( R_{-}/R_{+} \) range 0.145-6.92; that is, for chemically significant structures the attraction of each negative charge equally to the positive charges

\( (1) \) Carbon Acidity. 64. For paper 63 see: Streitwieser, A., Jr.; Juariisti, E. J. Org. Chem. 1982, 47, 768.

\( (2) \) Streitwieser, A., Jr.; Berke, C. M.; Robbers, K. J. Am. Chem. Soc. 1978, 100, 8271.

