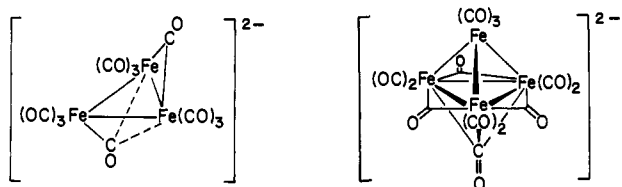


[$\alpha(^{13}\text{C}) = 3.55\text{G}$].¹³ Taken together with the ^{57}Fe data, these results identify IV as the radical anion $[\text{Fe}_3(\text{CO})_{12}]^-$,^{6e,14} in which all carbonyls are most probably rendered equivalent by a rapid intramolecular exchange.^{15,16}

Final confirmations of the identities of I, II, and III come from the observation that each of these species can be cleanly generated by the oxidation of the dianions $\text{Fe}_2(\text{CO})_8^{2-}$, $\text{Fe}_3(\text{CO})_{11}^{2-}$, and $\text{Fe}_4(\text{CO})_{13}^{2-}$, respectively, with 1 equiv of [ferrocenium] BF_4 or AgBF_4 in THF at -80°C .¹⁷ These results, together with the isotopic studies described above, leave little doubt that I, II, and III are the radical anions $\text{Fe}_2(\text{CO})_8^-$, $\text{Fe}_3(\text{CO})_{11}^-$, and $\text{Fe}_4(\text{C}-\text{O})_{13}^-$.¹⁸ Intensive efforts have so far failed to provide the ESR spectrum of the simplest member of this family, $\text{Fe}(\text{CO})_4^-$,¹⁹ probably because it rapidly dimerizes to the diamagnetic $\text{Fe}_2(\text{CO})_8^{2-}$ or combines with other iron carbonyl fragments. Interestingly, the oxidation of $\text{Fe}(\text{CO})_4^{2-}$ with equimolar solutions of the above oxidants as well as of $\text{Fe}(\text{CO})_5$ gives only the spectrum of I.

Our isotopic studies are consistent with structures for II and III which are closely related to those of the corresponding diamagnetic dianions II⁻ and III⁻ shown below.²⁰ Interestingly, III



cannot be fluxional on the ESR time scale at -80°C ; indeed, the relative intensities of the ^{13}C satellites for III (Figure 2B) are consistent with two sets of three equivalent carbonyls (16.2 G, 14.2 G), one set of six equivalent carbonyls (2.5 G), and one unique carbonyl (7.9 G), in complete analogy with the structure of its diamagnetic analogue III⁻. The two structures shown below,



possibly rapidly interconverting in solution,²¹ seem likely for I.

(13) The spectrum consists of a superposition of 13 lines for IV with 12 ^{13}C atoms (36.8%), 12 lines for IV with 11 ^{13}C atoms and 1 ^{12}C (38.4%) atoms, 11 lines for IV with 10 ^{13}C and 2 ^{12}C atoms (18.3%), etc. (cf. inset, Figure 3).

(14) See also A. M. Bond, P. A. Dawson, B. M. Peake, B. H. Robinson, and J. Simpson, *Inorg. Chem.*, **16**, 2199 (1977).

(15) The neutral species $\text{Fe}_3(\text{CO})_{12}$ is also highly fluxional: F. A. Cotton and D. L. Hunter, *Inorg. Chim. Acta*, **11**, L9 (1974).

(16) $\text{Fe}_3(\text{CO})_{12}^-$ is also obtained quantitatively by treating a dilute solution of $\text{Fe}_3(\text{CO})_{12}$ in THF with an equimolar solution of sodium naphthalide at -80°C . This reaction can be carried out on a preparative scale at ambient temperature. Use of 2 equiv of naphthalide followed by treatment with $[\text{PPN}]\text{Cl}$ produces analytically pure $[\text{PPN}]_2\text{Fe}_3(\text{CO})_{11}$.

(17) $\text{Na}_2\text{Fe}_2(\text{CO})_8$ was prepared by the method of ref 6d; $[\text{PPN}]_2\text{Fe}_3(\text{C}-\text{O})_{11}$ and $[\text{PPN}]_2\text{Fe}_4(\text{C}-\text{O})_{13}$ were prepared as described by H. A. Hodali and D. F. Shriver (*Inorg. Synth.*, **20**, 222 (1980); and to be published). Samples prepared by alternative methods gave equivalent results. All these salts, but particularly those of $\text{Fe}_2(\text{CO})_8^{2-}$, are difficult to prepare free of the paramagnetic anions discussed in this work.

(18) (a) The powder spectrum of II reveals a nearly symmetric g tensor with $g_1 = 2.0243$, $g_2 = 2.0321$, and $g_3 = 2.0921$. (b) It should be noted that the ^{57}Fe doublet for II in Figure 1B does not preclude a trinuclear structure for this species; the splitting due to the remaining ^{57}Fe atoms is simply not resolved because of the relatively broad line width.

(19) $\text{Fe}(\text{CO})_4^-$ has been detected by IR using matrix isolation techniques [J. K. Burdett, *Coord. Chem. Rev.*, **27**, 1 (1978); *Chem. Commun.*, 763 (1973)] and in the gas phase by ion cyclotron resonance [R. C. Dunbar, J. F. Ennever, and J. P. Fackler, Jr., *Inorg. Chem.*, **12**, 2734 (1973); J. H. Richardson, L. M. Stephenson, and J. I. Brauman, *J. Am. Chem. Soc.*, **96**, 3671 (1974); M. S. Foster and J. L. Beauchamp, *ibid.*, **97**, 4808 (1975)].

(20) (a) F. Y. Lo, G. Longoni, P. Chini, L. D. Lower, and L. F. Dahl, *J. Am. Chem. Soc.*, **102**, 7691 (1980); (b) R. J. Doedens and L. F. Dahl, *ibid.*, **88**, 4847 (1966).

The unbridged structure is that of $\text{Fe}_2(\text{CO})_8^{2-}$ in the solid state²² as well as of one of two isomers of matrix-isolated neutral $\text{Fe}_2(\text{CO})_8$, while the bridged structure is analogous to that proposed for the second isomer of $\text{Fe}_2(\text{CO})_8$.²³

Acknowledgment. We express our gratitude to Messrs. B. F. Gordon, D. J. Jones, and R. O. Balback for dedicated technical assistance, Professor D. F. Shriver for essential synthetic information, and Dr. A. Stout of the Pressure Chemical Co. for the synthesis of ^{13}C -labeled $\text{Fe}(\text{CO})_5$. Financial support to B.H. and R.L.H. was given by the R. A. Welch Foundation and to J.S.F. by the National Science Foundation and the Department of Energy.²⁴

(21) The spectrum of I derived from 92% ^{13}C -enriched $\text{Fe}(\text{CO})_5$ at -80°C is a single line of 7.7-G p-t-p width vs. 3.1-G width for I derived from normal $\text{Fe}(\text{CO})_5$ under strictly comparable conditions. This is consistent with several equivalent (rapidly exchanging) ^{13}C ligands but does not prove it. Work at lower temperatures in THF, at which I might be static on the ESR time scale, was hampered by severe line broadening.

(22) H. B. Chin, M. B. Smith, R. D. Wilson, and R. Bau, *J. Am. Chem. Soc.*, **96**, 5285 (1974).

(23) M. Poliakoff and J. J. Turner, *J. Chem. Soc. A*, 2403 (1971).

(24) NSF Grant 80-17045 and DOE Contract DE-AS05-80ER-10662.

ESR Study of Paramagnetic Iron Carbonyl Hydrides

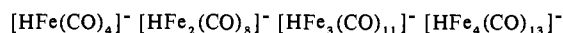
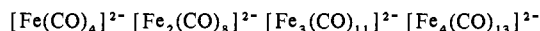
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In the preceding communication,¹ electron spin resonance (ESR) evidence was presented for a new series of iron carbonyl radical anions, I⁻–IV⁻, having one less electron than the corresponding well-known diamagnetic iron carbonylate dianions, I²⁻–IV²⁻. Iron also forms a parallel series of diamagnetic anionic



carbonyl hydrides, HI⁻–HIV⁻, which have found extensive applications in organic synthesis and homogeneous catalysis,² as well as a series of homologous neutral dihydrides, H₂I–H₂IV, which are relatively unstable and less studied. The anionic hydrides are strong reducing agents, and it is therefore possible that the series of neutral odd-electron hydrides, HI⁻–HIV⁻, formally the conjugate acids of I⁻–IV⁻, may also be important as reaction intermediates. We now present evidence supporting this conjecture and an ESR characterization of $\text{HFe}_2(\text{CO})_8^-$ (HII⁻) and $\text{HFe}_3(\text{CO})_{11}^-$ (HIII⁻). The latter provides, for the first time, ESR evidence for the very high mobility of CO ligands in a paramagnetic transition metal cluster.

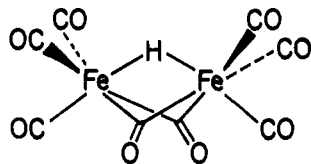
UV irradiation in an ESR cavity of dilute, olefin-free pentane solutions of $\text{Fe}(\text{CO})_5$ ($\sim 10^{-3}\text{M}$) below -100°C and under a pressure of ~ 30 atm of hydrogen³ gives rise to a spectrum of two narrow lines ($\Delta H \approx 1.3$ G) separated by 22.2 G with a g factor of 2.0120. The observation of a 1:1:1 triplet with a 3.3-G splitting and the same g factor in a similar experiment using deuterium establishes the formation of a paramagnetic iron carbonyl hydride.⁴

(1) P. J. Krusic, J. San Filippo, Jr., B. Hutchinson, R. L. Hance, and L. M. Daniels, *J. Am. Chem. Soc.*, preceding paper in this issue.

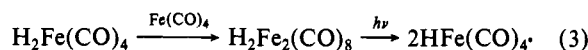
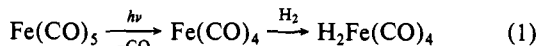
(2) For a review, see *Org. Synth. Metal Carbonyls*, **1**, 1 (1968).

(3) A thick-wall quartz tube with a special Teflon-plunger valve was used.

The same hydride is also observed when a dilute pentane solution of $\text{H}_2\text{Fe}(\text{CO})_4$ is similarly irradiated. A much higher concentration of this hydride is obtained if an approximately equimolar amount of $\text{Fe}(\text{CO})_5$ is added to the $\text{H}_2\text{Fe}(\text{CO})_4$ solution. Experiments with ^{57}Fe and ^{13}C labels described below require a hydride species with *two equivalent* Fe atoms and at least one set of *two equivalent* CO ligands which are static on the ESR time scale at -120°C . We conclude that this species is the $\text{HFe}_2(\text{CO})_8^\cdot$ radical probably isostructural with its diamagnetic anionic homologue HII^- whose X-ray structure⁵ is shown below.



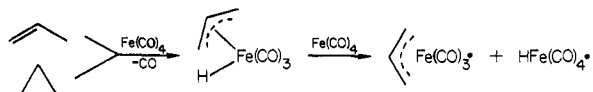
The results obtained with $\text{H}_2\text{Fe}(\text{CO})_4$ suggest that this hydride is initially formed in the photoreaction with H_2 by oxidative addition of the latter to the coordinatively unsaturated $\text{Fe}(\text{CO})_4$ produced in the primary photochemical act (reaction 1). We



propose that the 17-electron $\text{HFe}(\text{CO})_4^\cdot$ species is formed next perhaps by abstraction of a metal-bound hydrogen atom by the $\text{Fe}(\text{CO})_4$ fragment (reaction 2). Alternatively, $\text{Fe}(\text{CO})_4$ may combine with $\text{H}_2\text{Fe}(\text{CO})_4$ to give the diamagnetic $\text{H}_2\text{Fe}_2(\text{CO})_8$ which redistributes the hydrogen atoms and undergoes photochemical cleavage into two HI^\cdot radicals (reaction 3). The latter may then convert to the observed HII^\cdot by capturing an $\text{Fe}(\text{CO})_4$ fragment (reaction 4).

The $\text{HFe}_2(\text{CO})_8^\cdot$ radical is surprisingly ubiquitous. We detected it when dilute olefin-free pentane solutions of $\text{Fe}(\text{CO})_5$ (typically 10^{-3} M) were irradiated below -100°C in the presence of low concentrations (typically 0.05 M) of trialkylsilanes, alkyl and acyl halides with β hydrogens, aldehydes, simple cyclopropane derivatives, and several simple olefins. In each case, other organoiron radical species, generally thermally more stable, are also formed; these will be discussed elsewhere.

The photolysis of $\text{Fe}(\text{CO})_5$ in the presence of cyclopropane gives particularly intense spectra of HII^\cdot . Here we shall be concerned with this photochemical process only as a convenient source of HII^\cdot radicals for isotopic studies. Suffice it to say that, in addition to HII^\cdot , much more stable allyliron tricarbonyl radicals,⁶ in equilibrium with their diamagnetic dimers, are also formed. These radicals can also be obtained in high yields in similar experiments with propene (~ 0.05 M in pentane). We believe that both processes involve as a common intermediate the diamagnetic allyliron tricarbonyl hydride postulated before to explain the photochemical isomerization of terminal olefins under very similar conditions.⁷



The spectrum of HII^\cdot obtained from cyclopropane and $\text{Fe}(\text{CO})_5$ is shown in Figure 1A.⁸ The spectrum of DII^\cdot , obtained from

(4) The only paramagnetic hydride iron complexes known so far are $\text{HFe}(\text{dppe})_2^\cdot$ and $[\text{HFeCl}(\text{dppe})_2][\text{BF}_4]$ where $\text{dppe} = (\text{Ph}_2\text{PCH}_2)_2$; M. Gargano, P. Giannoccaro, M. Rossi, G. Vasopollo, and A. Sacco, *J. Chem. Soc., Dalton Trans.* 9 (1975).

(5) H. B. Chin and R. Bau, *Inorg. Chem.*, **17**, 2314 (1978).

(6) E. L. Muetterties, B. A. Sosinsky, and K. I. Zamaraev, *J. Am. Chem. Soc.*, **97**, 5299 (1975).

(7) M. A. Schroeder and M. S. Wrighton, *J. Am. Chem. Soc.*, **98**, 551 (1976).

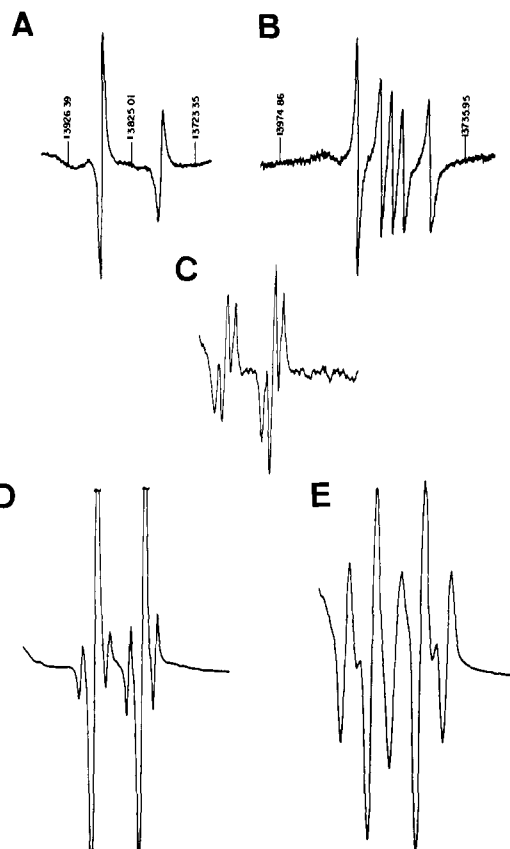


Figure 1. ESR spectra of various isotopically substituted $\text{HFe}_2(\text{CO})_8^\cdot$ species obtained by irradiating at -120°C (A) $\text{Fe}(\text{CO})_5$ in cyclopropane, (B) $\text{Fe}(\text{CO})_5$ in perdeuteriocyclopropane, (C) $^{57}\text{Fe}(\text{CO})_5$ in cyclopropane, (D) 10% ^{13}C -enriched $\text{Fe}(\text{CO})_5$ in cyclopropane, and (E) 92% ^{13}C -enriched $\text{Fe}(\text{CO})_5$ in cyclopropane. In C, D, and E the magnetic field increases from left to right.

cyclopropane- d_6 (>90% isotopic purity) is seen in Figure 1B. The concomitant formation of equivalent amounts of HII^\cdot , despite the paucity of available H atoms, indicates an unusually large isotope effect.

The spectrum in Figure 1C was obtained from cyclopropane and $^{57}\text{Fe}(\text{CO})_5$ ($\sim 93\%$ ^{57}Fe).¹ The additional triplet splitting (3.60 G) demands two equivalent ^{57}Fe atoms ($I = 1/2$). Cyclopropane and 10% ^{13}C -enriched $\text{Fe}(\text{CO})_5$ gave only one set of ^{13}C satellite doublets of 12.3 G (Figure 1D). Thus, either all CO ligands are equivalent or only one set of CO ligands gives resolvable hyperfine structure. The spectrum of Figure 1E obtained similarly from 92% ^{13}C -enriched $\text{Fe}(\text{CO})_5$ is consistent with the latter explanation. This spectrum consists of a doublet (22.2 G) of triplets (12.3 G) with the two innermost lines merging together. The triplet establishes the presence of two equivalent CO ligands.⁹ The greater line width in this spectrum ($\Delta H = 3.4$ G) is most likely caused by interactions with additional CO ligands whose number, unfortunately, cannot be deduced.

The $\text{HFe}_3(\text{CO})_{11}^\cdot$ radical can be easily made by oxidation of salts of the $\text{HFe}_3(\text{CO})_{11}^-$ anion with 1 equiv of AgBF_4 or $(\text{C}_5\text{H}_5)_2\text{FeBF}_4$ in THF at -80°C . This violet species is stable in-

(8) The downfield line of this doublet is broader than the upfield line; hence the different amplitudes. This effect is caused by the magnetic anisotropies of the species and insufficiently rapid molecular tumbling rates.

(9) It should be noted that HII^\cdot has two pairs of equivalent CO's. Thus, it is impossible to decide, on the basis of the present information, whether this unique pair of ^{13}C CO ligands, which interacts strongly with the unpaired electron, is the terminal or the bridging pair. However, our ^{13}C studies of a novel family of paramagnetic iron hydrides, with structures analogous to that shown for $\text{HFe}_2(\text{CO})_8^\cdot$ except that the two bridging CO ligands are replaced by bridging thiyil (SR) groups, show unambiguously that the pair of strongly interacting CO ligands is the terminal pair trans to the bridging hydrogen. The unpaired electron, then, resides in an extended V-shaped MO which comprises the two $d(z^2)$ orbitals of each octahedral iron and the orbitals of the terminal CO's along the octahedral axes.

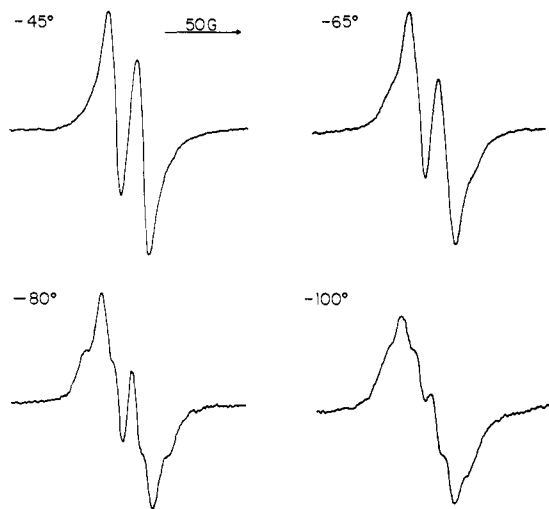


Figure 2. ESR spectra at four different temperatures of 92% ^{13}C -enriched $\text{HFe}_3(\text{CO})_{11}$ in THF.

definitely at this temperature but decays rapidly above -40°C . Its ESR spectrum is a doublet (18.4 G) with a line width of 5 G and a g factor of 2.0635.¹⁰ This species can also be obtained starting from 92% ^{13}C -enriched $\text{Fe}(\text{CO})_5$, as mentioned in the preceding communication (cf. ref 8).¹¹ At -45°C the presence of ^{13}C atoms merely broadens the line width. On lowering the temperature, however, the reversible spectral changes shown in Figure 2 are observed which are clearly caused by the slowing down of a rapid exchange of ^{13}C ligands between different sites. No further changes occur below -100°C , indicating that the cluster is now static on the ESR time scale. Although the resolution is wanting, the spectrum at -100°C clearly consists of six lines. It follows that each line of the original and invariant doublet is now split into a triplet with a splitting of ~ 6 G. Thus, the static $\text{HFe}_3(\text{CO})_{11}$ species has a set of two equivalent carbonyls which interact appreciably with the unpaired electron. Interestingly, the diamagnetic analogue HIII^- is also a highly fluxional molecule¹² whose slow-exchange ^{13}C NMR spectrum is consistent with its structure in the solid state.¹³ The latter is related to that of HII^- , shown above, by the replacement of one of the bridging carbonyls with an octahedral $\text{Fe}(\text{CO})_4$ group. The presence of two equivalent CO's in HIII^- does not exclude an isostructural relationship with HIII^- which has five equivalent pairs of CO's.¹⁴

Yet another very unstable paramagnetic hydride was observed in the low-temperature oxidations with AgBF_4 of THF solutions of I^- to which an equivalent of $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ had been added. The spectrum of this species at -80°C is a doublet of 23.9 G with a line width of ~ 5 G and a g factor of 2.0276. It is assigned provisionally to the paramagnetic hydride $\text{HFe}_4(\text{CO})_{13}$.¹⁵

Acknowledgment. I am very grateful to B. F. Gordon and D. J. Jones for technical assistance, Professor D. F. Shriver for a sample of $[\text{PPN}][\text{HFe}_3(\text{CO})_{11}]$ and useful comments, Professor J. San Filippo, Jr., and Dr. D. L. Thorn for informative discussions, Professor B. Hutchinson for a sample of $^{57}\text{Fe}(\text{CO})_5$, and Dr. William J. Cote for the synthesis of $\text{H}_2\text{Fe}(\text{CO})_4$.

(10) Expectedly, the deuterated analogue, $\text{DFe}_3(\text{CO})_{11}$, gave a single line ~ 10 G wide.

(11) In the same manner we have also obtained $\text{HFe}_3(\text{CO})_{11}$ from $^{57}\text{Fe}(\text{CO})_5$. Unfortunately, the ^{57}Fe hyperfine structure cannot be resolved, and the lines of the H doublet are simply broadened ($\Delta H \sim 7.2$ G).

(12) J. R. Wilkinson and L. J. Todd, *J. Organomet. Chem.*, **118**, 199 (1976).

(13) L. F. Dahl and J. F. Blount, *Inorg. Chem.*, **4**, 1373 (1965).

(14) We again suppose (cf. ref 9) that the strongly interacting pair of CO's is the terminal pair trans to the bridging H atom.

(15) Note Added in Proof: Similar oxidations of $[\text{PPN}][\text{HFe}_4(\text{CO})_{13}]$ failed so far to confirm this assignment perhaps because of the thermal instability of the paramagnetic hydride. I thank Professor D. F. Shriver and Dr. K. Whitmire for samples of $[\text{PPN}][\text{HFe}_4(\text{CO})_{13}]$.

A Systematically Designed Homogeneous Oscillating Reaction: The Arsenite-Iodate-Chlorite System

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The number of homogeneous chemical reactions known to exhibit sustained oscillations¹ is relatively small,² and all those reported thus far have either been discovered serendipitously or are variants or combinations of previously known oscillators.³ The recent surge of interest and progress in understanding the nature of chemical oscillation suggests that (a) the discovery of more fundamentally different oscillating reactions would be of major significance as a testing ground for general theories of dynamical behavior and (b) the time may be at hand when the criteria for oscillation are well enough understood to provide practical guidelines for the design of new oscillators. In this communication we present what we believe to be the first report of a systematically designed homogeneous oscillating reaction—the arsenite-iodate-chlorite system.

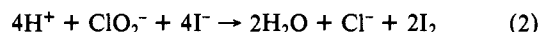
Although no necessary and sufficient set of conditions for chemical oscillation is known, several factors which enhance the likelihood of oscillation are clear. Maintenance of the system far from equilibrium is essential for sustained oscillations. Secondly, although it is not absolutely required if sufficiently complex feedback loops (e.g., cross-catalysis, autoinhibition) are present, autocatalysis is found in nearly all known chemical oscillators. Finally, it has been suggested⁴ that many systems which exhibit bistability should be capable of oscillation when subjected to an appropriate feedback.

In order to maintain our system far from equilibrium, we have carried out our experiments in a continuous flow stirred tank reactor (CSTR). We set out to choose an autocatalytic reaction which could give rise to two stable steady states under the same set of external constraints. For the autocatalytic system, we chose the arsenite-iodate reaction (eq 1), which is autocatalytic in



iodide.⁵ A study of this reaction in the CSTR⁶ showed that it is indeed bistable over a wide range of flow rates and inlet concentrations.

For oscillation production, the feedback reaction to be coupled to a bistable system need only produce an appropriate change in the region of stability of the steady states.⁴ However, iodide, the autocatalytic species in reaction 1, is also known to react with chlorite in reaction 2, which is autocatalytic in iodine.⁷ We



therefore chose to introduce chlorite into our system in an attempt to induce oscillation.

Figure 1 shows the spectrophotometric absorption at 460 nm, where both I_3^- and I_2 absorb significantly, and the potential of an iodide-sensitive electrode in the CSTR as a function of time. With a residence time of 400 s at 25°C and pH 2.35, oscillations, with periods between 15 s and 4 min, are observed over a range of $[\text{KIO}_3]_0$ from 24×10^{-3} to 80×10^{-3} M, $[\text{As}_2\text{O}_3]_0$ from 1.5×10^{-3} to 6×10^{-3} M, and $[\text{NaClO}_2]_0$ from 1.5×10^{-3} to 6×10^{-3} M. Note that the iodide concentration varies by a factor of more than 10^5 during each oscillation.

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