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(19) **Note Added in Proof**: Recent NMR studies indicate that the substrate oxygens probably lie in the second coordination sphere of the metal (Rosevear, P. R.; Sellin, S.; Mannervik, B.; Mildvan, A. S. *Fed. Proc., Fed. Am. Soc. Exp. Biol.* **1982**, *41*, 1152).

Minimal Bromate Oscillator: Bromate-Bromide-Catalyst[1]

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While the first homogeneous oscillating chemical reaction discovered, the Bray reaction,[3] is an iodate-containing system, bromate oscillators, especially the prototype Belousov-Zhabotinsky reaction,[4] have until recently dominated both the experimental study and mechanistic understanding of chemical oscillation. Noyes[5] has distinguished five classes of "bromate-driven oscillators", four of which consist of bromate, bromide, a redox couple, and an organic reducing substrate, and a fifth "uncatalyzed" class in which the organic substrate performs some of the functions of the metal as well. The Field-Körös-Noyes[6] and derived mechanisms[7] give predictions in excellent qualitative agreement with experimental results on these systems, though the details of some reactions involving the organic substrate remain a mystery.[8]

Essentially quantitative agreement between theory and experiment has been obtained for the conditions under which bistability is found in a stirred tank reactor (CSTR) when only bromate, bromide, and cerium are present.[9] These calculations also predict the existence of a very narrow region of small-amplitude oscillations in this system.[10] The first experimental search for these oscillations was, however, unsuccessful.[11]

We report here the discovery, within an extraordinarily narrow range of conditions, of oscillations in a CSTR containing bromate, bromide, and cerous or manganous ions. This finding is of major importance not only because it lends further support to the mechanism but also because, as we discuss below and elsewhere,[12] it greatly enlarges the scope of bromate oscillation.

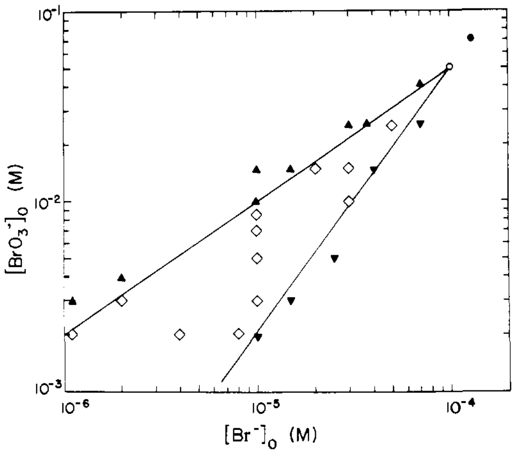

Figure 1. Section of the phase diagram in the $[BrO_3^-]_0$-$[Br^-]_0$ plane with flow rate $k_0 = 0.0128$ s^{-1}, $[Mn^{2+}]_0 = 1.02 \times 10^{-4}$ M, $[H_2SO_4] = 1.5$ M, $T = 25$ °C: (▲) high potential (low bromide) state; (▼) low potential (high bromide) state; (◇) bistability; (○) oscillation (critical point); (●) critical point (oscillatory composition) when Mn^{2+} is replaced by 1.02×10^{-4} M Ce^{3+} and all other constraints as above.

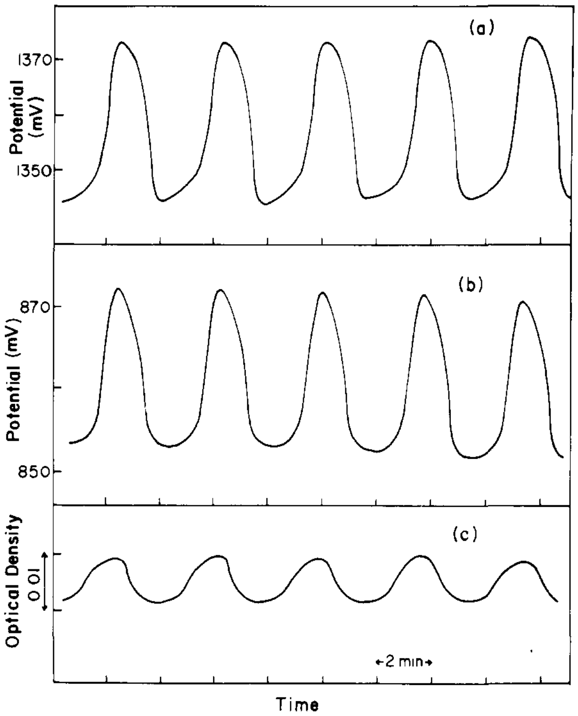

Figure 2. Oscillations at the critical point ○ of the phase diagram in Figure 1 ($[BrO_3^-]_0 = 0.048$ M, $[Br^-]_0 = 9.8 \times 10^{-5}$ M): (a) potential of Pt electrode; (b) potential of bromide selective electrode (uncalibrated, but $[Br^-] < 10^{-7}$ M); (c) absorbance at 350 nm (primarily due to Mn(III) and Br_2, though absorbance oscillations at Br_2 absorption maximum at 390 nm are considerably smaller).

Experiments were performed in two thermally regulated CSTR's of volumes 21 and 28.7 cm^3. The reactors, which have been described elsewhere,[13] were modified to eliminate any air space over the reaction mixture. The potentials of a platinum redox electrode and a bromide selective electrode against a mercurous sulfate reference electrode as well as the optical density at various wavelengths were continuously recorded.

In Figure 1 we show the phase diagram at fixed flow rate, temperature, and input flux of Mn^{2+}, for the bromate-bromide-manganous system in the $[BrO_3^-]_0$-$[Br^-]_0$ plane. A relatively broad region of bistability narrows as the bromate and bromide input concentrations are increased until it disappears at the critical point $[BrO_3^-]_0 = 0.048$ M, $[Br^-]_0 = 9.8 \times 10^{-5}$ M. With manganous replaced by cerous ion, the critical point occurs at $[BrO_3^-]_0 = 0.072$ M, $[Br^-]_0 = 1.22 \times 10^{-4}$ M. In an *extremely narrow*

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(1) Part 10 in the series Systematic Design of Chemical Oscillators. Part 9: Grant, J. L.; De Kepper, P.; Epstein, I. R.; Kustin, K.; Orbân, M. *Inorg. Chem.*, in press.

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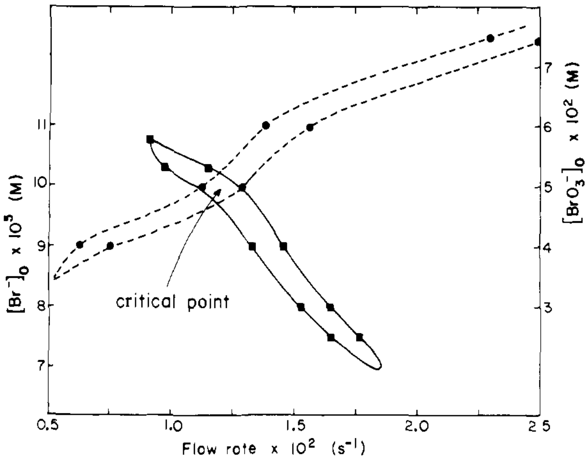

Figure 3. Phase diagram showing how region of oscillation shifts as constraints are varied in the region of the critical point. Solid line encloses region of oscillation as $[Br^-]_0$ and k_0 vary at fixed $[BrO_3^-]_0 = 0.05$ M. Dashed line encloses oscillatory region as $[BrO_3^-]_0$ and k_0 vary at $[Br^-]_0 = 1.0 \times 10^{-4}$ M. Other constraints as in Figure 1.

region about these points, small amplitude oscillations occur as shown in Figure 2.

If any of the constraints, $[BrO_3^-]_0$, $[Br^-]_0$, or flow rate k_0, is changed by as little as a few percent away from the critical point, oscillations cease and can be regained only by making a compensating change in one of the other constraints. The manner in which the oscillation region shifts with the constraints is shown in Figure 3.

The oscillator discovered here can function only in a flow reactor, since the necessary generation of bromide (process C in Noyes' scheme[5]), which occurs via the organic substrate in all previously found bromate oscillators, is replaced here by an input flow of bromide. The bromate–bromide–catalyst system is the simplest bromate oscillator yet found (or likely to be found). It may be called the minimal or basic bromate oscillator. As we show elsewhere,[12] it forms the cornerstone of a larger systematic classification of bromate oscillators, of which Noyes' five classes constitute one subsystem. It opens the way, with use of the cross-shaped diagram technique,[14] to developing a new class of bromate–bromide–catalyst–oxidizing substrate oscillators, which we shall discuss in a future publication. It is significant that though the range of bromate oscillators is considerably larger than contained in Noyes' classification,[5] the basic mechanistic description remains valid.

From a mechanistic point of view, the present system is probably the best understood chemical oscillator. The tiny region and small amplitude of oscillation agree beautifully with Bar-Eli's calculation.[10] The possibility of such behavior in the immediate region of a critical point has also been predicted from more general models.[15,16] Experimentally, however, this system constitutes perhaps the most difficult oscillator to work with, since very small differences in the constraints, even those involved in changing nominally identical input tubes in the flow system, can significantly shift the region of oscillation.

With the discovery of this basic bromate oscillator and of other oxyhalogen oscillators in flow systems, it appears that the development of a unified classification of not only bromate but chlorite and iodate oscillators as well is well within reach.

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Registry No. BrO_3^-, 15541-45-4; Br^-, 24959-67-9.

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A New Method for the Identification of the Origin of Natural Products. Quantitative ^2H NMR at the Natural Abundance Level Applied to the Characterization of Anetholes

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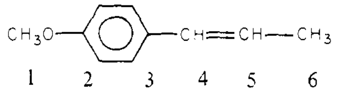
We have shown by high-field ^2H NMR spectrometry at the natural abundance level that very spectacular differences exist in the internal distribution of ^2H in organic molecules. This phenomenon has been exemplified in particular by the case of ethyl[1] and vinyl[2] derivatives. We show in this study of various anethole samples the potential of this new method as a very powerful tool for the characterization and identification of natural products from different origins.

It is known that significant variations exist in the overall deuterium content of organic molecules, and mass spectrometry has been successfully used to measure this total ^2H content in various species.[3] Unfortunately this technique requires relatively complicated and tedious preparation of the samples, and moreover it does not provide direct information about the internal distribution of ^2H. Although attempts have been made to obtain this information by means of complex chemical transformations of the sample,[4] to our knowledge no unambiguous conclusions have been drawn, and the interpretation of the variation in the overall ^2H contents in terms of chemical and biochemical mechanisms has usually remained speculative. It is therefore particularly interesting from both the analytical and mechanistic points of view to have a method at our disposal that is capable of providing direct access to the deuterium content of each specific molecular site.

The NMR spectra of ^2H at the natural abundance level obtained at 38.897 MHz with proton noise decoupling for various samples of trans anethole are composed of six lines characterized by the following chemical shift values.



	1	2	3	4	5	6
ppm/Me_4Si	3.75	6.80	7.23	6.28	6.08	1.83

As a result of the low natural abundance of ^2H (156×10^{-6}) with respect to ^1H, the probability of having bideuterated species is negligible, and the signals observed for the anethole samples correspond respectively to the six molecular species I–VI monodeuterated in sites 1–6. We shall define the intramolecular distribution of ^2H by means of the molar fractions $f(i)$ of molecules I–VI. These parameters can be derived from the area $S(i)$ of the individual deuterium signals on condition that suitable experimental parameters are selected.[5] Moreover in order to compare the ^2H content in a given site of a given anethole sample to that of the same site in another sample, we inserted coaxially into the measuring cell a tube containing a reference substance (CH_3CN).

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