Chiral Symmetry Breaking in Crystallization: The Role of Convection

T. Buhse,[2] D. Durand,[1] D. Kondepudi,[1,*] J. Laudadio,[1] and S. Spilker[1]

[1]*Department of Chemistry, Wake Forest University, Winston-Salem, North Carolina 27109-7486*
[2]*Centro de Investigaciones Quimicas, Universidad Autonoma del Estado de Morelos, Avenida Universidad 1001,*
Colonia Chamilpa, C.P. 62210, Cuernavaca, Morelos, Mexico

Chiral symmetry breaking in stirred crystallization of sodium chlorate ($NaClO_3$) occurs via the production of secondary crystals from a single "mother crystal." Martin, Tharrington, and Wu [Phys. Rev. Lett. **77**, 2826 (1996)] investigated this phenomenon and concluded that it was mechanical crushing of a crystal by the stir bar, not convection, that produces secondary crystals from a single crystal. Here we report the generation of secondary crystals of sodium chlorate when a saturated solution of sodium chlorate is simply made to flow over a sodium bromate ($NaBrO_3$) crystal. This clearly shows that fluid flows alone can generate and disperse secondary nuclei.

Introduction. — The generation and propagation of chiral asymmetry at various levels, from the level of elementary particles to asymmetric morphologies of plants and animals, is of general interest. The ubiquity of chiral asymmetry stands in stark contrast to the paucity of chemical processes that spontaneously generate large chiral asymmetry. Crystallization, however, is an exception: here chiral autocatalysis is easily accomplished in stirred crystallization through secondary nucleation, the production of more crystal nuclei by a crystal. We were able to realize chiral symmetry breaking in stirred crystallization of $NaClO_3$ and $NaBrO_3$ [1,2] and in the stirred crystallization of 1-1' binaphthyl from its melt [3]. Though $NaClO_3$ is not a chiral molecule, crystals of $NaClO_3$ are optically active. The levo (l) or dextro (d) rotatory crystals could easily be identified with a pair of polarizers. In a typical crystallization of this compound in a static solution, a nearly statistically equal number of l and d crystals are obtained [1,2,4] as expected, though significant deviations from expected binomial distribution have been noted [5]. If the crystallization is performed while the solution is constantly stirred, however, one observes almost all (often more than 98%) l or d crystals in each crystallization. Each stirred crystallization produces either almost all l or almost all d crystals randomly. If N_l and N_d are the number of l and d crystals, respectively, the crystal enantiomeric excess (CEE) is defined as $(N_l - N_d)/(N_l + N_d)$. If a large number of stirred crystallizations are performed, the resulting probability distribution of CEE, or percent of l crystals, is bimodal with peaks close to 0 and 100%. Also, we showed that the probability distribution of the CEE makes a transition from a monomodal to a bimodal distribution as the stirring rpm increases [6] from 0 to 1000 rpm. This result was reproduced by Martin *et al.* [7] in a somewhat different experimental setting. Chiral symmetry breaking in stirred crystallization of $NaClO_3$ was observed some years ago [1,2,6], but the exact mechanism underlying this process is yet to be fully understood.

The most important factor in chiral symmetry breaking is secondary nucleation. Secondary nucleation is the chirally autocatalytic process by which a "mother crystal" generates secondary crystals at a rapid rate if the solution is stirred; in the case of $NaClO_3$, an l or d crystal can generate thousands of crystals with similar chirality in a few minutes. In this Letter, we address an important issue raised by Martin *et al.* [7] in response to our previous experiments and a computer simulation of this process of Metcalfe and Ottino [8]: the role of convection. Are the secondary crystals generated through mechanical crushing of the mother crystal by the stir bar, or can secondary crystals also be produced due to convection? Martin *et al.* concluded that mechanical crushing of the mother crystal is the source of secondary crystals and that the role of convection is questionable. In our experiments we have noted that a collision between a crystal and the stir bar does generate a cloud of secondary nuclei, and a video observation of this phenomenon was reported by McBride and Carter [9]. But this is not the only mechanism. Here we report a series of experiments which show that fluid flow can indeed disperse secondary crystals generated near the surface of the "seed" or "mother" crystal, an important aspect that any theory of secondary nucleation must explain. In our experiments, secondary nuclei of $NaClO_3$ are generated from a $NaBrO_3$ crystal solely due to fluid convection.

Empirical laws for the rates of secondary nucleation can be found in chemical engineering literature and the rate depends on stirring rpm [10–16]. The dependence of secondary nucleation on the rpm is, at least partially, due to convection. Numerous times we have observed the generation of secondary nuclei in stirred systems without any noticeable solid-solid contact between a crystal and the stir bar. Furthermore, earlier studies [17] seem to indicate that convection alone is capable of generating secondary nuclei from a seed crystal. To determine the relevance of convection for the observed symmetry breaking, we have conducted a systematic study of the generation of

secondary nuclei which is entirely through fluid flow. Our objective was to determine if the surface of a chiral seed crystal is capable of catalyzing the production of crystal nuclei that are chirally identical to itself, which then are dispersed by convection. In fact, we used $NaBrO_3$ (whose crystal structure is isomorphic to that of $NaClO_3$) as the seed crystal which catalyzes the production of $NaClO_3$ crystals in a chirally selective manner.

Generation of secondary nuclei and their dispersal due to fluid flow.—Our study consists of the following sets of experiments. In the first series of crystallizations, as shown in Fig. 1, saturated $NaClO_3$ solution at 23 °C (of concentration 0.829 g $NaClO_3$ per 1 g H_2O) was made to flow over l or d-$NaBrO_3$ crystals and into a Petri dish containing supersaturated $NaClO_3$ solution. The solution in the Petri dishes was made supersaturated by about 4 °C by placing the dishes on a plate cooled with circulating water. In each run, two Petri dishes were seeded with l-$NaBrO_3$, two were seeded with d-$NaBrO_3$ crystal, and crystallization in one "control" Petri dish was performed without any seeding. In each case, the l or d seed was first thoroughly washed in distilled water to remove any dust that might be present—a procedure often used in such experiments [18]. Then it was held over each Petri dish with a pair of tweezers, and 5.0 ml of saturated $NaClO_3$ solution was dropped over the seed using a syringe fitted with a 40 μm membrane filter to eliminate nuclei that may act as a source for secondary nucleation. Studies on secondary nucleation have shown that, for significant generation of secondary nuclei, the seed must have a minimum size [13]. This minimum size is in the range 100–500 μm for the compounds studied [13]. For $NaClO_3$, we found [2] that numerical simulation that fit the experimental data well required a minimum seed size of 900 μm. Thus, crystals capable of generating secondary nuclei, if they existed at all, have been eliminated by the filter. On the other hand, the critical nucleation size is generally much lower than 40 μm. Thus, crystals smaller than 40 μm, if they existed, might pass through the membrane filter, but these must be insignificant in number compared to the secondary nuclei generated by the seed, as the results show.
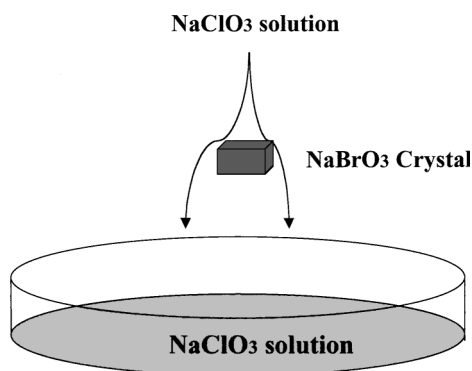

FIG. 1.   Chirally selective crystallization of $NaClO_3$ using seeds of $NaBrO_3$ crystals.

Flowing over the seed, the solution from the syringe dripped into the Petri dish containing 5.0 ml of the supersaturated $NaClO_3$ solution. If any crystal nuclei were produced in the vicinity of the $NaBrO_3$ seed crystal, they would be transported into the Petri dish. (As described below, the same procedure of washing the seed produced no secondary nuclei in a static solution indicating that no "crystal dust" was introduced into the system by the $NaBrO_3$ seed.) Similarly, 5.0 ml of the saturated solution was also dropped in the control Petri dish using an identical syringe fitted with a membrane filter. In addition, a series of crystallizations using achiral NaCl crystals in the place of $NaBrO_3$ were also performed. The same saturated solution was used for all Petri dishes. A separate l- or d-$NaBrO_3$ crystal was used as a seed for each Petri dish. In about 40–60 min after this procedure, a large number of small crystals could be observed in the Petri dishes for which a seed was used, but it took much longer, often many hours, before visible crystals appeared in the control dish. Furthermore, the number of crystals in the control dish was significantly smaller than the seeded Petri dishes. The crystals thus obtained were allowed to grow to a size of a few millimeters—which took about one or two days. A random sample of 100 crystals was taken from each Petri dish and the number of l and d crystals was counted using a pair of polarizers.

Results and discussion.—If $NaBrO_3$ seeds can catalyze the production of $NaClO_3$, one should observe a strong correlation between the seed and the percentage of l crystals in each Petri dish for which a seed was used. As summarized in Fig. 2(a), we indeed see a strong correlation between the chirality of the seed and the crystal enantiomeric excess found in each Petri dish. One important aspect of this correlation must be noted, however. $NaClO_3$ and $NaBrO_3$ crystals with identical chiral crystal structure in terms of their atomic arrangement, which we shall denote by L or D (in contrast to optical activity which is denoted by l or d) the corresponding optical activities at visible wavelengths are opposite in sign [19]. Thus, a levo-rotatory l-$NaBrO_3$ crystal catalyzes the production of dextro-rotatory d-$NaClO_3$ crystals and vice versa; stated in terms of the atomic arrangements or crystal structure, L-$NaBrO_3$ catalyzes L-$NaClO_3$ and D-$NaBrO_3$ catalyzes D-$NaClO_3$. This is the reason why a larger percentage of l-$NaClO_3$ crystals were found in crystallizations seeded with d-$NaBrO_3$ crystals and vice versa. The mean percentage of l crystals for the d-$NaBrO_3$-seeded crystallizations was found to be 84.9% while that of the l-$NaBrO_3$-seeded crystallizations was 18.6%. The percentage of l crystals found in the control Petri dishes, for which no $NaBrO_3$ seeds were used, and those found when achiral NaCl seeds were used are summarized in Figs. 2(b) and 2(c); the corresponding means of the percentages of l crystals are 48.6% and 52.2%, respectively.

From the above results it is clear that chirally autocatalytic generation of the crystal nuclei occurs in the vicinity of a chiral crystal. By using washed $NaBrO_3$ crystals as
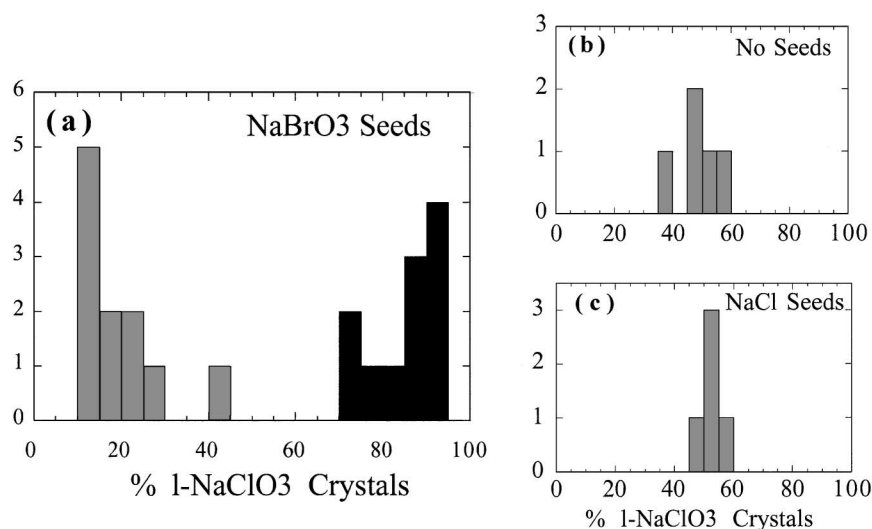
FIG. 2. (a) Histograms of percentage of l-NaClO$_3$ crystals obtained with l- and d-NaBrO$_3$ seeds are shown by light and dark bars, respectively. The optical activities (denoted by l or d) of NaClO$_3$ and NaBrO$_3$ crystals with identical chiral atomic arrangements are opposite in sign. Hence the inverse correlation between the optical activity of the NaBrO$_3$ seed and the percentage of l-NaClO$_3$ crystals. (b) Histogram of percentage of l crystals obtained with no seed. (c) Histogram of percentage of l crystals obtained with achiral NaCl seed.

seeds, we ensured that all the NaClO$_3$ crystals came from the solution and not the seed. Furthermore, because the NaClO$_3$ solution that was dripped over the NaBrO$_3$ and NaCl seeds is saturated with Na$^+$ ions, the crystals that were used as seeds do not dissolve in the solution and no NaBrO$_3$ or NaCl is transferred into the Petri dishes.

To investigate the importance of the flow or convection of the saturated solution in dispersing the secondary nuclei generated at the surface of the NaBrO$_3$ seed, we performed a series of NaClO$_3$ crystallizations in Petri dishes in which washed NaBrO$_3$ seeds were placed gently to avoid fluid movement as much as possible. If any crystal dust was introduced through the NaBrO$_3$ seed, the dust would have generated a cluster of crystals around the seed and the chirality of these crystals would have been strongly correlated with that of the NaBrO$_3$ seed. But no such clustering was observed. All conditions are identical to those used in the above crystallization except for introduction of the NaBrO$_3$ seeds. The percentage of l crystals obtained in these crystallizations are summarized in Fig. 3. These results show that the seed has no noticeable effect on the CEE when there is no flow of the solution. The mean percentage of l crystals was 51.6% for the l seed and 52% for the d seed. Comparison of Fig. 2(a) and Fig. 3 clearly shows that fluid convection makes an enormous difference for the dispersal of secondary nuclei. In these experiments we also noticed that NaClO$_3$ crystal growth occurred on the NaBrO$_3$ seeds, but the absence of any cluster of crystals near the seed showed that the washed seed did not introduce dust that could act as nucleation sites. The mean percentage of l crystals being close to 50 further supports this point; if dust was introduced along with the seed, there should be a strong correlation with the chirality of the seed.

Fluid flow clearly plays an important role in the secondary nucleation observed in our experiments. However, as noted earlier by McBride and Carter [9], mechanical contact between a crystal and the stir bar does generate secondary crystals, but this may not necessarily be due to the crushing of a crystal. Indeed, as McBride and Carter noted (and we have observed it in our lab as well), a single col-

lision between a crystal and the stir bar generates a cloud of secondary crystals as if thousands of small nuclei have been dispersed from the vicinity of the crystal. In these crystallizations that take place in a 100 ml beaker, a crystal that forms at the liquid-air interface drops when it can no longer be supported by surface tension and sometimes hits the stir bar. Within a few minutes after this event, a cloud of tiny crystals is generated. The crystal that hits the stir bar is not crushed into small pieces; however, the impact could have broken a large number of dendrites from it.
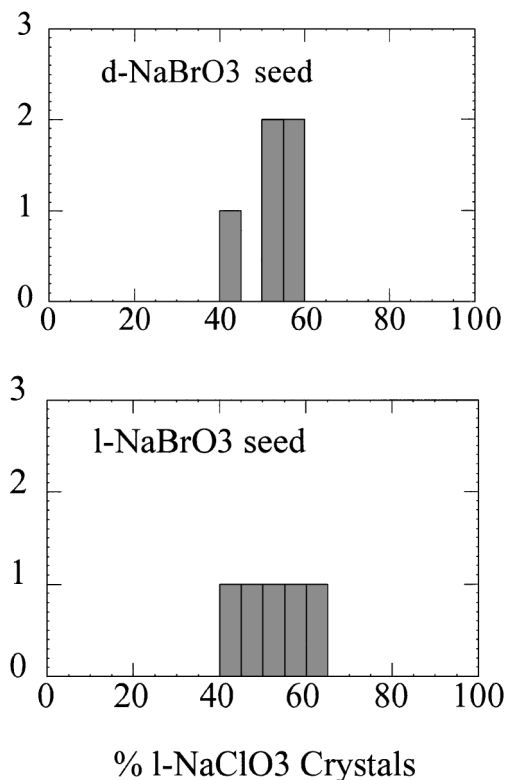

FIG. 3. Histograms of percentages of l-NaClO$_3$ crystals in crystallization of NaClO$_3$ with l- and d-NaBrO$_3$ seeds with no fluid flow.

More recently, after a very detailed study, Qian and Botsaris [18] have concluded that at high supersaturation (more than 8 °C supercooling) large clusters ("embryos") could form in the vicinity of the seed crystal and become nuclei [20]. These nuclei can be dispersed through fluid convection. These results suggest that breaking and dispersal of dendrites due to convection, while likely, may not be the only mechanism for the production of secondary nuclei. Qian and Botsaris have shown that, as the supersaturation increases, the probability that the secondary nuclei have the same structure as the seed decrease. They found that, for a NaClO$_3$ seed, in the range 3–6 °C of supercooling, nearly 100% of the secondary crystals generated have the same chirality as the seed; if the supersaturation exceeds 6 °C, the fraction of chirally similar secondary crystals is smaller and it varies randomly. Qian and Botsaris also note that the microscopic conditions, such as local supersaturation near the seed, factors which are difficult to control, may strongly influence the rate of production and the chirality of the secondary nuclei. These observations explain many of the features in our data including the stochastic nature of the percentage of l crystals observed in Fig. 2(a) and the lack of 100% correlation between the chirality of the seed and the secondary nuclei generated from it.

Finally, we comment on the difference between our setup used to study spontaneous chiral symmetry breaking [1,2] and that used by Martin *et al.* [7]. Our system contains 60–80 ml of solution in a 100 ml beaker with a 1.25 cm Teflon stir bar rotating at 1100 rpm, while Martin *et al.* used a thin layer of solution (5.0 and 7.5 ml in a Petri dish of 5.0 cm diameter) and floated their stir bar. The floated stir bar was magnetically rotated at a maximum of 60 rpm. In their system, crystals could perhaps be trapped under the stir bar, but in ours it is virtually impossible for the same to happen. Our results do not necessarily contradict theirs but only underscore the importance of convection in our setup in which chiral symmetry breaking was observed and reported [1,2,6]. Martin *et al.* also report that when the solution was "stirred" by blowing N$_2$ gas at the surface, the percentage of l crystals was nearly 50. This result is easily explained. Blowing N$_2$ gas at the liquid surface causes rapid evaporation and formation of a large number of crystal nuclei at the surface. During such rapid crystallization, an equal number of l and d crystals are generated. In fact, a similar result can be obtained by bubbling a gas through a saturated solution of NaClO$_3$. Crystals are quickly generated at the liquid/gas interface of the bubbles; the resulting percentage of l or d crystals is nearly 50 [18].

Conclusion. — We see that, though crystal–stir bar collision is a mechanism for the generation of secondary nuclei, the role of convection is also important: convection does disperse secondary nuclei generated in the vicinity of a crystal. Whether convection is mechanically breaking off dendrites or also dispersing crystal nuclei formed in the vicinity of the seed crystal, as Qian and Botsaris suggest, remains to be clarified. In either case, our ex-periments have shown that convection alone does generate secondary nuclei. When secondary nuclei of NaClO$_3$ are generated from NaBrO$_3$ seed, it is possible that dendrites grown heteroepitaxially are broken and dispersed due to convection. Clearly secondary nucleation and fluid flow are important in explaining the observed chiral symmetry breaking in stirred crystallization. The exact nature of the mechanism that generates secondary nuclei now becomes a very interesting question, a new theory that has recently been proposed by Qian and Botsaris [20]. The chiral selectivity that seems to occur in the vicinity of a solid surface may have important consequences not only for chiral crystals, but also for chemical reactions.

*Author to whom correspondence should be addressed.

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