

Resolving a Controversy: The Non-Classical Ion Debate

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In 1961, Herbert Brown—who would eventually go on to win the Nobel Prize in Chemistry (1979)—presented a controversial paper to the London Chemical Society. In this paper he suggested that appeals to non-classical carbonium ion intermediates in the explanation of solvolysis results were not being made with, “the same care and same sound experimental basis as that which is customary in other areas of experimental organic chemistry.”¹ This paper set off what Brown referred to as a “holy war” to establish the legitimacy of explanations employing non-classical carbocations. Brown and his followers fought back, both criticizing the evidence presented in favor of non-classical ions and offering alternative explanations.² The ensuing controversy lasted for over twenty years and involved many of the era’s most respected physical organic chemists (including George Olah, arguing against Brown, who also won the Nobel Prize in Chemistry (1994)). By the time the controversy sputtered to a halt (with Brown still a holdout) in the early 1980s, a tremendous amount of intellectual energy, resources, and invective had been invested in resolving an issue that was not crucial to progress in either physical organic chemistry generally or even the subfield of carbocation chemistry.³

In earlier phases of my research, I focused on the class of chemical reactions at the center of the Non-classical Ion Debate—the solvolysis of 2-Norbornyl systems. I used explanations of properties of these systems that arose in the Non-classical Ion Debate, as well as the participants’ reflections on these explanations, to bring out several distinctive characteristics of the explanatory and theoretical structure of organic chemistry. Most of the explanations in organic chemistry are contrastive; that is, one tries to understand the reactive behavior of a chemical system relative to a contrasting system (frequently, a standard or more basic reaction). In simple cases, there is only one relevant structural feature that distinguishes the system of interest from the contrasting system, in which case it is easy to explain the differences in chemical behavior between the systems. In more complicated systems, however, multiple structural features may contribute to the relevant behavioral differences. Such systems bring out an additional, distinctive feature of the explanations in organic chemistry: they seek to explain complex cases by composing the effects of structural features initially identified and understood in simple cases. Because the (quantitative) impact of a particular structural feature on the chemical behavior of a system is generally sensitive to the chemical environment (or to the rest of the structure in which the feature appears) it is frequently not possible to (quantitatively) predict how the effects of multiple structural features will compose. As a result, many explanations of properties of complex systems in organic chemistry are *ex post facto* attempts to identify which structural features are primarily responsible for particular facts about chemical behavior, attempts that proceed by judicious choice of relevantly analogous, contrasting chemical systems.

The debate over how to explain properties of the solvolysis of 2-Norbornyl systems exposes the limitations of the contrastive, compositional strategy employed in the explanations of organic chemistry. The participants in the debate were unable to reach a consensus, at least in part,

because they were unable to agree about which contrasting chemical systems effectively established the extent of a structural feature's contributions to the behavior of 2-Norbornyl systems. To some extent, this was due to distinctive features of the norbornyl system, but it also reveals the heuristic character of the strategies employed by organic chemists in trying to understand the behavior of complex systems. These strategies have their origins in attempts to support the synthesis of complex compounds, and so they must be robust and applicable in novel situations. The cost of this robustness seems to be the potential for controversy in certain ambiguous cases, like that of the norbornyl system. Reflection on the Non-classical Ion Debate has provided, therefore, a window on the economics of the explanatory strategies of organic chemists.

Eventually, physical organic chemists left the non-classical ion debate behind. Almost all were convinced that an appeal to non-classical ions was appropriate in the norbornyl system. Brown was virtually alone as a holdout. As Brock has suggested that this was due to, "a battery of physical evidence from chromatography, infrared and nuclear magnetic resonance spectroscopy."⁴ Much of this evidence did not bear directly on the solvolysis reactions that had originally been the subject of the controversy, but it did establish that there was a broad range of chemical environments in which appeals to non-classical ions, and in particular non-classical norbornyl cations, were plausible and appropriate. Brown was sometimes able to offer rational resistance to this new evidence by invoking the difference in chemical environment between the original norbornyl system and these various chemical contexts, but the range of situations in which he could resist non-classical ions progressively narrowed. As a result, the force of his original criticism—that there was something systematically amiss in explanations that invoked non-classical ions—was diminished, even if rational resistance was still plausible in the particular context on which the debate had originally centered. The solvolysis of norbornyl systems was significant to organic chemists insofar as it was a barometer for the appropriateness of appeals to non-classical ions in the explanations of the discipline. Once the appropriateness of such appeals had been established in other ways, the norbornyl system was no longer significant. Brown might still defend his interpretation of the particular case, but this case no longer had the broader implications that had originally made it important. The resolution of the non-classical ion debate is thus an example of how a scientific community can get beyond a controversy by draining it of its significance, rather than by settling on some definitive experiment or evidence that awards victory to one side or the other. Though heuristic explanatory approaches like that of organic chemistry may leave room for theoretical questions which cannot be resolved on the basis of empirical evidence, this does not mean that empirical evidence is incapable of resolving the resultant controversies.

Notes and References:

- 1) Bartlett (ed.), 1965, *Non-Classical Ions*. W. A. Benjamin. New York. Brown's paper is reprinted with commentary on pp. 437-62. The quote is from p. 454.
- 2) See Herbert C. Brown, 1977, *The Nonclassical Ion Problem*. Plenum Press. New York. The quote is from p. 8.
- 3) See "Carbocations" by E. Arnett, T. Hofelich, and G. Schriver in *Reactive Intermediates* Vol. 3,

M. Jones and R. Moss (eds.), John Wiley and Sons. New York: 1985. Arnett et. al. claim:

“Another clue to the marginal relevance of the nonclassical ion controversy is the fact that the chemistry of carbocations has progressed so successfully without its resolution” (p. 191).

4)See William H. Brock, 2000, *The Chemical Tree: A History of Chemistry*. Norton and Company. New York. The quote is from p. 568.