

EDITORIAL
Happy Birthday to Joe Bunnett



Joseph F. Bunnett, the founding editor of *Accounts of Chemical Research*, turned 90 this November. As many readers may remember, the launching of *Accounts* in 1968 was Joe Bunnett's brainchild. His idea that a journal devoted to short, concise, and critical articles offering easy-to-read overviews of basic research in all areas of chemistry would be highly desirable proved to be visionary. Indeed, under his strong leadership for 20 years, the journal flourished, its standing as measured by impact factors and Journal Citation Reports has been high from the start and steadily increased further over time. One notable feature that made *Accounts* special during his editorship was his frequent editorials on topics of high relevance to the scientific community at large, including comments about ethics in science and publications, quality in research, "acronymia," education versus training, the defense of scientific hypotheses, and many more.

Joe Bunnett's contributions to chemistry of course go well beyond his editorship of *Accounts*. During his distinguished career as one of the most nationally and internationally respected physical organic chemists he made his mark not only in publishing seminal papers in the area of organic reaction mechanisms but also as an educator and leader. I personally benefited from his unusual gift and charisma as a teacher while I was a visiting graduate student in his laboratory at Brown University in 1964. I also personally witnessed and admired his leadership qualities as he was building up the Chemistry Department at the

University of California at Santa Cruz in the late 1960s and the 1970s and helped shape the unique character of our campus.

Joe Bunnett has received numerous honors in recognition of his many outstanding contributions to our understanding of chemical reactions. They include his election as fellow of the American Academy of Arts and Sciences and of the American Association for the Advancement of Science and his election as Honorary Member of numerous European and South American chemical societies, of the Pharmaceutical Society of Japan, and foremost, he was the recipient of the 1992 James Flack Norris Award in Physical Organic Chemistry.

In order to fully appreciate Joe Bunnett's scientific contributions, one needs to realize that when he started his independent research in organic reaction mechanisms in 1946, the understanding of mechanisms was quite limited and rather primitive by today's standards. For example, it was commonly believed that nucleophilic aromatic substitution occurred by the single-step S_N2 mechanism, that E2-eliminations occurred via a transition state fixed with respect to bond orders, and that the Zucker–Hammett hypothesis was sufficient for the quantitative treatment of reactions in sulfuric acid solutions; also little was known about the role of radical anions in reaction mechanisms. The drastic revision of these primitive ideas, and others, that occurred since then stems in large measure from the research of Joseph Bunnett.

A complication in the retrospective evaluation of a long career is that some of the important early achievements seem mundane today. They appear in textbooks, often without mention of who discovered them. But the very fact that they become common knowledge testifies to their importance. Examination of the circumstances of these discoveries reveals that they were not obvious at the time but were often challenged until years of further research led to their general acceptance.

Such is the case with several of Bunnett's most important contributions. The first major one was his recognition that the most common mechanism of nucleophilic aromatic substitution occurs by a two-step mechanism (S_NAr) rather

than an S_N2 -type mechanism. His original proposal in 1951 was initially strongly challenged by other investigators but, after a series of compelling papers, was gradually accepted. I feel personally very honored to have carried out some of the most conclusive experiments regarding this mechanism while working in Bunnett's laboratory at Brown University.

Another seminal contribution was Bunnett's recognition in 1962 of factors that determine the variable character of the transition state of E2-eliminations. Building on Bunnett's insights led to the visualization of the variable features of E2 transition states by means of More O'Ferrall–Jencks diagrams that are now commonly used in the teaching of variable transition state theory. Thus, Bunnett's ideas are taught but usually not attributed to him.

In the 1970s, Bunnett discovered that nucleophilic substitution in many aromatic systems with or without substituents occurred by a radical anion mechanism he called $S_{RN}1$. Subsequent work in his laboratory further validated this mechanism and expanded its scope to include a wide variety of aromatic substitutions. Numerous other workers demonstrated its value for achieving important synthetic objectives.

While the foregoing may be regarded as his major contributions, several other discoveries in his laboratory were highly novel and significant but space limitations do not allow me to elaborate. Nevertheless, I would like to make two additional points. One relates to the unusual clarity and sheer elegance of his writing in all his publications. The other refers to a particular paper that provides a glimpse into an unconventional and witty side of his personality: it is a paper written in Greek style verse! (*J. Org. Chem.*, **1971**, *36*, 184)

Finally, Bunnett also played a major role within the International Union of Pure and Applied Chemistry (IUPAC); he was a member and then chair of the Commission on Physical Organic Chemistry and eventually chair of the IUPAC Organic Chemistry Division Committee. Furthermore, after his retirement, he became actively involved in affairs relating to the destruction and detection of chemical warfare agents. Specifically he was chairman of the IUPAC Task Force on the Scientific Aspects of the Destruction of Chemical Warfare Agents and later chairman of the IUPAC Committee on Chemical Weapons Destruction.

My colleagues at UC Santa Cruz and I are particularly happy that Joe Bunnett continues to participate in our departmental activities and weekly seminars, and we honor his scientific contributions at the annual Bunnett Lecture presented by some of the most eminent people in the field. His great mentorship to students and young faculty,

something I experienced personally, his devotion to building a department and university, his scientific discoveries, and his stewardship of science and chemistry, including the creation of this journal, are a legacy that enriches us all.

Happy birthday, Joe!

Claude F. Bernasconi

Guest Editor

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