

ticularly useful in teaching general chemistry. Students, they argue, will get used to it from their earliest experience to mechanistic problems and thus will go on to use it. I strongly disagree. General chemistry should be a joyful experience of the miraculous world of chemistry and could do well without excessive exposure to either the Schrödinger equation or the new IUPAC symbolism of reaction mechanisms. The latter may find useful application by specialized practitioners of mechanisms, but I see no compelling reason to discard the widely used Ingold system. Change for the sake of change does not always necessarily represent progress. Time-proven units, classifications, and namings tend to survive even IUPAC's attempts. Calories are still around and are making a strong comeback, despite all attempts telling us the advantages of using joules. Let's not rush to condemn Ingold's symbols for substitution, elimination, and addition reactions. Particularly, let's save our students from further confusion

of nomenclature and instead concentrate our efforts on emphasizing the real meaning of chemistry.⁴

(4) One of the referees stated that my Commentary represents what one might call the reactionary position with regard to the IUPAC proposal and its main argument is that we should stick with the old system just because we are used to it. He added that this is a puzzling point of view for someone who was a chief campaigner for changing the nomenclature of carbocations. I would better describe my views as conservative. I believe in conserving established values. If I am accused of this, I take full responsibility. The naming of carbocations (in analogy to carbanions) as the generic name for all positive ions of carbon compounds emerged from the necessity of the experimental realization that different types of these ions exist (trivalent carbenium ions and pentacoordinate (or higher coordinate) carbonium ions). The general carbocation naming avoids the necessity of previous detailed knowledge of the structure of any ion.

George A. Olah

Loker Hydrocarbon Research Institute and
Department of Chemistry
University of Southern California
Los Angeles, California 90089

Responses to Commentary by Professor Olah

In my opinion, the most important problem in chemical reaction mechanisms today is to make a clear distinction between *appearance* and *reality*.

The *appearance* of the rate-limiting transition state of a reaction is characterized by measurements of the effects of substituents, isotopes, solvent, temperature, and pressure on the reaction rate. These measurements can provide evidence that supports a dissociative or an associative transition state, for example. The overall *nature* of a chemical reaction may be defined by the transformations that take place and the kinetic order of the reaction, as described by the Ingold nomenclature. The *mechanism* of a reaction, on the other hand, is defined by the nature, the number, and the sequence of the steps in the reaction. The steps represent the formation or further reaction of intermediate species that have a significant lifetime. The number of steps can usually be defined if an intermediate species is taken to be a structure with a lifetime that permits several vibrations, i.e., $> \sim 10^{-13}$ s.

Reaction mechanisms have an integral number of steps and an integral reaction order; a reaction can have one step or two steps, but not one and a half steps. Thus, it is usually misleading to speak of a spectrum, a continuum, or merging of mechanisms. These terms generally refer to the appearance of a transition state, not a reaction mechanism. It is, of course, possible that a reaction can occur concurrently through two different mechanisms, but this is described better as a mixture than as a merging of mechanisms.

The appearance of the transition state cannot be relied on for the diagnosis of a reaction mechanism. For example, solvolysis and substitution reactions of monosubstituted phosphate monoanions and dianions proceed through a dissociative transition state, and for many years it was widely believed that they proceed through a monomeric metaphosphate monoanion intermediate. In fact, there is evidence that in most nucleophilic solvents they proceed by a one-step concerted mechanism (A_ND_N) with a dissociative transition state that resembles the metaphosphate ion.¹ Similarly, solvolysis and substitution at carbon can

proceed through a concerted mechanism (A_ND_N) with a dissociative transition state that resembles a carbenium ion; such reactions can easily be (and have been) mistakenly assigned to a stepwise S_N1 mechanism.²

George Olah expresses the view that will undoubtedly be held by many, perhaps most chemists, when first confronted with a new system. Why, indeed, should a "tried and true" nomenclature be abandoned and a new system learned? As indicated above, the original or a modified Ingold system need not be abandoned; rather it should be used to describe the nature of reactions, the purpose for which it was designed.

A new system is needed because the Ingold system does not describe reaction mechanisms and its use has led to ambiguity in the interpretation of mechanisms. For example, Ingold himself described the S_N2 reaction as concerted (A_ND_N);³ it "contains only one stage, in which two molecules simultaneously undergo covalency change", but more recently a stepwise " S_N2 intermediate" mechanism ($D_N^*A_N$) has been proposed.⁴ The term " S_N2 " does not distinguish between these different mechanisms. In order to save our students from the existing confusion of nomenclature, it is essential to use a nomenclature that distinguishes the nature of a reaction from its mechanism and that describes reaction mechanisms clearly and unambiguously.

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William P. Jencks

Graduate Department of Biochemistry
Brandeis University
Waltham, Massachusetts 02254-9110