

Citation Classics

Russell G A, Janzen E G & Strom E T. Electron-transfer processes. 1. The scope of the reaction between carbanions or nitranions and unsaturated electron acceptors. *J. Amer. Chem. Soc.* **86**:1807-14, 1964.

This paper documents by electron spin resonance (ESR) techniques the widespread occurrence of electron transfer between mono- and di-anions, wherein the negative charge is centered on carbon or nitrogen, and a wide variety of unsaturated organic compounds, particularly those containing nitro, nitroso, azo or carbonyl functional groups, or easily reducible saturated compounds such as peroxides, disulfides, and alkyl or aryl halides. Electron transfer was also observed using a variety of organo metallic reagents as the donors and various polynuclear- or hetero-aromatic compounds as the electron acceptors. [The SC[®] indicates that this paper was cited 330 times in the period 1964-1977.]

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"Ed Janzen, Tom Strom and I are indeed flattered to have one of our publications included in the SC[®] most-cited paper list. Frankly, at the time this diffuse paper was written in 1963, the editor and I had some reservations about its suitability. We had in hand some rather nice examples of the occurrence of electron transfer (ET) in organic systems. However, I felt that these hard-core examples of ET between diamagnetic substrates did not place in proper perspective the scope or implications of this process. Therefore, I tried to gather together various scraps from the older literature, various predictions about when ET was likely to occur, and a variety of illustrations from our own work to form a sort of summary paper as our initial full publication. Our basic premise was that one electron oxidation or reduction of an unsaturated organic system did not require classical agents such as the alkali or other metals, radical anions, transition metal ions, or electrode surfaces. Instead, diamagnetic carbanions ($\equiv \text{C}^-$) or nitranions ($> \text{N}^-$) could

spontaneously ET to an unsaturated system (π) to yield a free radical ($\equiv \text{C}$ or $> \text{N} \cdot$) and the radical anion derived from the unsaturate (π^-), while carbocations ($\equiv \text{C}^+$) or dications could accept an electron from easily oxidized molecules. One variation in the overall scheme was to increase the electron affinity of the acceptor by photo-excitation. In many ways we simply extended basic concepts of inorganic and electroanalytical chemistry to the organic sphere. However, I feel we did perform a service for subsequent workers in this area by providing a key reference or benchmark from which they could develop their own discussions. I think the paper added another dimension to the organic chemist's outlook. At the time this paper appeared many chemists thought of reactions of organic anions or cations only as being electrophilic or nucleophilic in nature. Electrons were presumed to move in pairs, and perhaps it was a small but important step forward to demonstrate that electrons do not always move as pairs. In fact, I think the editor in accepting this paper missed this point completely but accepted the paper because he felt it had something to do with dihydropyridine chemistry, a subject of considerable interest but one which involves mainly electron pair chemistry.

"The circumstance which led me to the somewhat presumptuous attempt to summarize a diffuse area of chemistry in a research article can be traced to our application of new techniques and instrumentation. In the early 1960's my group was one of the first to apply electron spin resonance (ESR) spectroscopy to the study of organic reactions. We soon recognized that some of the standard reactions of organic chemistry required a new mechanistic formulation involving ET. One such process described in a later paper in this series was the base-catalyzed coupling of nitrosobenzene and phenylhydroxylamine to yield azoxybenzene. Our appreciation of ET led us to look for new examples of this process possessing utility. Thus, we subsequently discovered the ET chain mechanism for the substitution reaction between carbanions and a -substituted nitro alkanes. This process, dubbed the S_{RN}1 reaction, was later shown by others to be an important general replacement reaction in a variety of aromatic systems."