

Radiation Chemistry and Electric Discharge Chemistry:
Comparison and Contrast.

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* The Radiation Laboratory of the University of Notre Dame is operated under contract with the U. S. Atomic Energy Commission. This is AEC document number COO-38-511.

In radiation chemistry the customary situation is that a charged particle with energy in the MeV range is slowed down in matter and, in the course of such deceleration, excites some molecules and ionizes others. The ultimate fate of the initial charged particle is of little consequence compared to the many processes which it initiates but that initial particle is actually responsible for initial excitations and ionizations which amount to about one-quarter of the total number of such processes. The corollary statement is that about three-quarters of all the effects observed are attributable to the action of secondary (and, to a very small extent, tertiary) charged particles. Roughly, these particles have initial energy, ϵ_i , averaging about 75 eV.

The secondary charged particles can cause further ionizations (in addition to excitations) only so long as they have energy, ϵ , in excess of the ionization potential, I , of the species which they traverse. A convenient value for I is about 10 eV. When ϵ becomes $< I$, the only processes which can occur significant for radiation chemistry are electronic excitations to singlet or triplet states. When ϵ becomes < 5 eV the major portion of the excitations are optically disallowed (i. e., mainly triplet). For radiation chemistry about $\frac{3}{4} \times \frac{5}{75}$ or 5% of all the phenomena are initiated by particles with about that amount of energy.

In electric discharge processes, irrespective of the voltage employed the electrons start with about zero energy and rarely attain an energy in excess of 5 eV and much more rarely in excess of the ionization potential. It has been one of the important problems of electric discharge chemistry to determine how molecules are excited to chemically active levels and how ionized species are produced. According to some theoretical views most of the electrons cause optically forbidden excitations on the first opportunity and it might appear that chemical effects simply could not be observed. Nevertheless, they are observed and the fact must be that a significant number of molecules are excited to sufficiently high states so that chemistry results. Furthermore, some of them, in number adequate for maintenance of the discharge, are excited up to ionization potentials. Thus, in this case, ϵ_i is initially approximately zero and might appear not to exceed very low energies; e. g., ϵ_t , corresponding to the lowest triplet state. Yet, high excitations and ionizations do occur.

Two views may be employed to account for this dilemma. The theory presented is oversimplified and electrons in significant quantity attain energies in excess of 7 eV. Alternatively, it was suggested initially by Magee and Burton¹ that electric discharge chemistry is characterized by a series of successive excitations by low-energy electrons in optically forbidden steps to higher and higher levels with ultimate attainment of levels adequate for production of a chemical effect - or even of ionization.

The role of thermal energy is somewhat different in the two fields. In discharge chemistry a local temperature may be raised as high as 1000°C, whereas the usual dosage level used in the basic research of radiation chemistry is so low that the temperature increase can be of the order of a few degrees C even if the entire energy input is converted to thermal energy. This difference is not a trivial one, because thermal

energy and electronic energy (in the forms of excitation or ionization) do not exist as independent sources of energy for chemical reactions; the effect arising from a combination of the two forms of energy is not a simple sum of the two effects when each source acts alone. The detail of the interaction between thermal and electronic energies is not known. The qualitative picture, however, is fairly well understood. Namely, the rate of energy conversion from the electronic to the thermal form (radiationless transition or energy degradation) increases as the temperature increases. Thus, the process has the characteristics of an explosive chain reaction.

The main reason for this difference is attributable to the difference in the spatial distribution of excited and ionized species initially formed in each field. In radiation chemistry the distribution is more or less uniform as a natural consequence of the high penetrating power of the impinging radiation and highly random nature of the energy loss processes. The local inhomogeneities of energy deposition are submicroscopic in size and cannot be conveniently conceived as local regions of abnormal temperature. The "hot spot" idea has little significance in modern theories of the usual radiation chemistry. On the other hand, in a discharge tube, electronic excitation and ionization are somewhat confined to certain parts of the tube (negative glow and positive column). Since electronic excitation processes are generally accompanied by vibrational excitation (because of the Franck-Condon principle), the temperatures of these regions are also expected to be higher than those of the rest of the system. The direct transfer of electron energy to vibrational or translational motions of molecules can be ignored.

On the other hand, the coexistence of high temperature and high density of excitation is not really unique to electric-discharge chemistry. Under extremely high dose rate with certain charged species (particularly heavy particles such as fission fragments), it is probable that a similar situation has significance in the radiation chemistry of unusual systems.

A rather obvious feature of radiation chemistry, which cannot be found in discharge chemistry is the fact that the impinging energy is theoretically sufficient to excite the molecule to a level where multiple-bond dissociation and multiple ionization are possible. These effects have indeed been observed, but their contribution to the total chemical effect of high-energy radiation turns out to be negligible. The role of highly excited states or excited ionized states in the physical aspect of radiation chemistry (energy or charge transfer processes) is far from being negligible. By contrast, it would appear that lower excited states alone are the initial products of excitation in electric-discharge chemistry. In the latter case higher states appear to result from successive excitation exclusively and, under certain conditions of chemical reactivity, any presumptive substantial role of such states in the chemistry of discharge processes can be completely excluded - at least, on a speculative basis.

Radiation chemistry may be studied in systems of any degree of aggregation from highly attenuated matter (as in interstellar space) to liquids or solids under high compression. Studies in electric-discharge

chemistry seem limited essentially to gases or to interfaces involving gaseous systems. In radiation chemistry a major question is why, in spite of the initially high energies involved, the chemical effects are as specific as observed. In electric-discharge chemistry, by contrast, a very important question is why chemical effects are at all observed and why they are observed in the high yields reported.

References

1. Milton Burton and John L. Magee, *J. Chem. Phys.*, 23, 2194 (1955).
2. F. Dessauer, *Z. Physik*, 20, 288 (1923).