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SOME GENERAL PRINCIPLES IN THE RADIATION CHEMISTRY
OF ORGANIC COMPOUNDS*

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Donald J. Metz
Brookhaven National Laboratory
Upton, N. Y.

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INTRODUCTION

The scope of this talk, as indicated by the title, is quite broad and comprehensive, and a complete discussion of all the aspects of the problem would take us far longer than the time allotted will permit. At the outset, then, I would like to present a very short outline of what I intend to discuss, and how we shall approach the several sub-topics.

Firstly, I would like to set the field of radiation chemistry in perspective, by briefly discussing the similarities and differences between it, as a distinct discipline, and the more firmly established field of photochemistry. Secondly, we will discuss the results from two different approaches to studying the radiation chemistry of organic compounds. The first approach depends upon a detailed study of the nature and yield of products formed as a result of radiolysis, and the effect of the nature of the irradiated substrate, and its physical state, on these quantities. The second approach attempts to identify the nature of the reactive intermediates which result from the radiation process and which are responsible for the end products formed. Finally, I would like to dwell a bit on the latter topic--the identification of intermediates--

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as studied by a uniquely suited chemical reaction--vinyl polymerization.

RADIATION CHEMISTRY VS. PHOTOCHEMISTRY

To set the stage, then, let us begin with a comparison of radiation chemistry and photochemistry. The one basic similarity between the two fields of study is that the over-all processes that occur can be summarized by analagous simplified schemes:

Photochemistry:

Radiation Chemistry:

Unfortunately, it is at this point that the similarity between the two fields ends for all practical purposes.

In the first place, whereas photochemistry is confined to the interaction between matter and electromagnetic radiation (of several electron volts), radiation chemistry involves the study of the interactions between matter and both particulate radiations--alpha + beta particles, accelerated electrons, protons, etc., and electromagnetic radiations--hard X-rays and gamma rays--all involving energies from several kilovolts to several million electron volts. Both qualitatively and quantitatively, then, one might expect differences.

The wide spectrum encompassed by radiation chemistry is much too broad to be fully discussed here. So, I will confine my remarks to high energy electromagnetic radiations, namely, gamma rays. Although this greatly narrows the field, it in no way reduces our subsequent discussion to merely an extension of photochemistry. We still must contend with the large energy difference between the photons of photochemistry and the photons of radiation chemistry. Figure 1 is a graphical representation of this difference.

Basically, where does this energy difference lead? In photochemistry, as is well known, the interaction between the incident photon and a molecule is governed by certain quantum mechanical selection rules. A photon either possesses or does not possess the proper energy to excite an electron and lead to the formation of reactive intermediates, usually free radicals or atoms. No such restrictions exist in the interaction of a high energy gamma ray and a molecule. Indeed, although several modes of interaction exist, the most important ones for the gamma ray energies usually employed in radiation chemistry studies and in materials of low atomic number are electronic excitation and ionization by a Compton scattering process. The latter can be treated as a "classical" billiard ball collision between a photon and an electron which is essentially free. The recoil electron from the Compton process is sufficiently energetic to cause further excitations and ionizations within the material. These higher order interactions occur

Figure 1

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until the electrons approach thermal energies, at which point they are captured by either an initially formed positive particle (or some fragment thereof) or a neutral molecule.

When recombination occurs between a thermal electron and a positively charged fragment, the resulting neutral molecule is excited by an amount of energy equal at least to the ionization potential of the molecule formed. This excited molecule may then dissociate homolytically, to form free radicals, or heterolytically, to produce ions. These reactions are summarized in the simplified scheme below:

Thus, in general, the interaction of an organic molecule with a high energy gamma ray produces ions, free radicals and excited molecules. The determination of the relative importance of these species is the field that will be touched on in the latter portion of this talk.

Another consequence of the energy difference in the photons employed in photochemistry and radiation chemistry is the much higher degree of specificity achieved in the former field. In many instances, it is possible in a photochemical decomposition to select a photon of just the proper energy to break a specific bond in the molecules of the substrate. Again, this is based on the quantum mechanical selection rules governing the interaction.

On the other hand, a gamma ray photon of, let's say, one million electron volts, can interact with any orbital electron of a molecule, and generally will interact on a statistical basis. Thus, the initial interaction is essentially a random process. Just how random the subsequent chemical reactions are is the subject of investigation of the stoichiometric relations between products and reactant.

EFFECT OF CHEMICAL STRUCTURE ON RADIATION CHEMISTRY

Some of the earliest studies in the radiation chemistry of hydrocarbons seemed to indicate that not only was the initial ionization process a statistically governed one, but that also the ratio of hydrogen to methane formed, the two principle products, were related to the relative number of hydrogen atoms and end methyl groups, with the ratio decreasing with increasing branching of the hydrocarbon.

In the radiation of primary alcohols, although hydrogen is the principle gaseous product formed, there is found a preponderance of vicinal glycol in the higher molecular products, indicating a somewhat preferential removal of the alpha-hydrogen atom followed by recombination of two of the residual fragments. Clearly this is an indication of a certain degree of specificity.

Again, investigation of a homologous series of fatty acids reveals that the relative amount of carbon dioxide found in the gaseous products is essentially independent of the length of the chain. This apparently is another indication of a channeling of energy to a specific site within the molecule.

Indeed, although radiolysis at first appeared to be a very random, non-specific process, each new investigation leads to the further realization that, although nowhere near specific as photochemistry, perhaps a better description of radiation chemistry is that it is less specific, but not entirely non-specific.

Some of the generalizations that can be made concerning the preferential scission of certain bonds in molecules, arranged by chemical class, are collected and presented in Table I.⁽¹⁾ Thus, some easily detectable degree of specificity does certainly exist. To what extent such generalizations can be further refined cannot at this time be predicted.

Another generalization which appears to be true is that aromatic compounds are more resistant to radiation damage than aliphatic compounds. In addition, the number of products formed during the

Table I

Main Bonds Broken in Radiolysis
of Pure Organic Compounds.

Compound Type	Main Attack Site	Approx. G _{-M}
Hydrocarbons:		
Saturated	C-H, C-C	6-9
Unsaturated	C-H, C-C; polymerization or cross linking	11-10,000
Aromatic	C-H; side chain C-C	0.2-1
Alcohols	H-COH, C-COH	3-6
Ethers	C-H, C-OR	~7
Aldehydes & Ketones	C-H, C-C=O	~7
Esters	C-H, C-C(=O)OR	~4
Carboxylic Acids	C-H, C-COOH	~5
Halogen Compounds:		
Fluorides	C-H, C-C	~3
Others	C-H, C-X	~3

radiolysis of an aromatic compound is generally fewer than in aliphatic compounds. What little solace this latter statement affords can be seen by looking at Figures 2⁽²⁾ and 3⁽²⁾, which show the vapor phase chromatograms of a sample of irradiated toluene indicating, respectively, the products of lower molecular weight and higher molecular weight than the starting material. Table II⁽²⁾ presents the identities of those products which have been successfully identified, and their relative radiolytic yields. Obviously, the complete analysis and product identification of even a simple aromatic system presents formidable problems.

The detailed study of the effects of radiation chemistry on organic compounds has been made possible by the increasing availability of sensitive analytical tools, including vapor phase chromatography, mass spectrometry and isotopic substitution. With an increasing amount of effort going into this type of research, we can expect an ever increasing understanding of what chemical and physical factors affect the radiolysis of these materials.

IDENTIFICATION OF INTERMEDIATES

Many studies, both experimental and theoretical, have been directed towards the reactive intermediates responsible for the formation of the stable products that result from the radiolysis process. At first glance one might expect that all three species--excited molecules, ions and free radicals--might contribute to the over-all reactions.

Figure 2

Figure 3

Table II

Products and Yields from Toluene Radiolysis

Product ^a	G x 10 ³ ^b	G _{I₂} x 10 ³ ^b	Previous Data ^c G x 10 ³
C ₅ - C ₆ saturated and unsaturated (3-10)	0.62	N. D.	
4 methyl-1-cyclohexene (25)	0.83	N. D.	
1 methyl-1-cyclohexene (28)			
cis 1,2 dimethylcyclohexene (29)	3.65	N. D.	
dimethylcyclohexenes (31)	8.90	1.5	
benzene (32)	18.80	*	14.0
methylcyclohexadiene (38)	62.30	30.0	
ethylbenzene	1.2	N. D.	1.1
para-xylene	1.0	N. D.	0.9
meta-xylene	1.5	N. D.	1.1
ortho-xylene	0.9	N. D.	1.1
2,2 dimethylbiphenyl (2)	2.7	3.2	3.3
benzylmethylcyclohexadiene (9)	23.9	N. D.	18.0
2,3 dimethylbiphenyl (12)	43.2	11.0	9.0
3 methyldiphenylmethane (14)	9.7	9.5	16.5
2,4 dimethylbiphenyl (15)	5.8	5.7	5.5
4 methyldiphenylmethane (17)	10.2	*	7.5
3 methylbiphenyl (18)	5.3	*	0.2
bibenzyl (21)	71.5	3.5	41.0
3,3 dimethylbiphenyl (23)	7.1	2.0	6.5
3,4 dimethylbiphenyl (25)	8.1	4.0	7.5
4,4 dimethylbiphenyl (27)	2.1	1.0	2.2

The numbers in parentheses refer to the peak number on the chromatograms; those with retention times less than toluene (Figure 2) appearing above the dotted line and those with retention times greater than toluene (Figure 3) below.

N. D. - not detectable.

* - not determined due to interference in chromatograph.

^a see page 7.

^b yield obtained at 50°C.

^c data from Hoigne and Gaumann ref. 1, yields obtained at 25°C.

Several investigations of reactions in the gaseous and the liquid state have led to the conclusion that, under the proper conditions, energy can be transferred from an upper lying, excited level of molecule A to a lower lying level of molecule B when a mixture of the two are irradiated. Although this type of energy transfer process probably does occur, the role of excited molecules in radiation chemistry, especially in terms of the total amount of energy deposited in the system, has usually been relegated to a secondary one. Thus, most attention has been focused on the reactions of ions and free radicals.

In gas phase radiolyses, reactions have frequently been attributed to ionic intermediates. This is especially true in studies made in the rather artificial atmosphere of the mass spectrometer. However, just as many gas phase studies have been best interpreted in terms of free radical intermediates.

This tendency--to explain reactions in terms of free radicals--has been even more universally applied in the radiolysis of materials in the liquid and solid states. This has been justified both on the basis of postulated reaction schemes and theoretical treatments of the early stages of radiation events in condensed media. It has been argued, on both these grounds, that the life-times of ions are so short, and charge neutralization leading to homolytic

scission so efficient, that only radicals were left to carry out the subsequent chemical reactions leading to product formation.

Water and aqueous systems, one of the earliest and most extensively studied areas of radiation chemistry, were interpreted as reacting principally through the formation of hydrogen atoms and hydroxyl radicals. Theoretical calculations⁽³⁾ for water explained this behavior and even "predicted" it on the basis that there was, on the average, insufficient kinetic energy to allow most of the electrons ejected by the higher generation ionization processes to escape their parent conjugate ions, even in a medium of as high a dielectric constant as water. What chance, then, did the analogous electrons have in hydrocarbon systems?

Now, one of the intensively studied areas in organic radiation chemistry, going back around twelve to fifteen years ago, was that of radiation induced vinyl polymerizations. In retrospect, these materials were also very excellent diagnostic tools to study the question of the existence of ions and/or free radicals in condensed media, since the relative abilities of them to respond to anionic, cationic and free radical initiation by chemical species was already well known. In addition, the long kinetic chain lengths displayed by these systems are capable of expanding the time scale over which the intermediates "live" and, in addition, produce a relatively large amount of product per initiation event.

Table III is a brief condensation of some of the kinetic characteristics displayed by vinyl monomers under several different types of initiation. Although it is by no means comprehensive, it will serve as a background for the discussion which follows.

All liquid vinyl monomers, which polymerize in such a fashion that the polymer produced remains soluble in the monomer, when irradiated--using gamma rays, electrons, etc.--displayed such characteristics as are listed under ultraviolet initiation in Table III. Not only that, but when other criteria were applied, such as the composition of copolymers formed in a copolymerization initiated by high energy radiation, again the free radical nature of the initiating species was confirmed. When several monomers which were known not to polymerize readily by conventional free radical initiation were irradiated, no appreciable polymer was formed.

Apparently, then, the question was settled.

Then, in 1957-58, Davison, Pinner and Worrall⁽⁴⁾ reported that dry isobutylene, at temperatures below room temperature, would polymerize under the influence of gamma radiation. In addition, as far as preliminary work went, the process had all the earmarks of an ionic polymerization. Needless to say, this caused a stir and, what is more important, caused a re-investigation of the entire field.

TABLE III

Broad Kinetic Characteristics of
Vinyl Polymerizations

	Free Radical		Carbonium Ion
	Chemical	Photochemical	Chemical
$R_p \propto$	$[\text{Cat}]^{\frac{1}{2}}$	$[\text{I}]^{\frac{1}{2}}$	$[\text{Cat}]^1$
$\bar{P}_n \propto$	$[\text{Cat}]^{-\frac{1}{2}}$	$[\text{I}]^{-\frac{1}{2}}$	$[\text{Cat}]^0$
$(E_a)_p$	21-23 kcal/mole	6-8 kcal/mole	-(0-3) kcal/mole
$(E_a)_m$	-(7-9)kcal/mole	10-12 kcal/mole	-(0-3) kcal/mole

Several different approaches were followed: (1) the radiation of highly polar monomers in highly polar solvents;^(5,6) (2) the radiation of monomers, with or without solvents of high dielectric constant, at low temperature;^(7,9) (3) the addition of solid second phases;^(7,8) and (4) the study of highly purified and dried monomers which normally would not polymerize by free radical catalysts, such as isobutylene,⁽¹⁰⁾ beta-pinene,⁽¹¹⁾ and alpha methyl styrene.⁽¹²⁻¹⁵⁾

It is this latter approach, and some of its startling discoveries, that I would like to dwell on now, especially the results which have been recently obtained in a rather unexpected quarter, namely, the monomer styrene.

Now, all the results on the radiation induced polymerization of liquid styrene pointed unequivocally to the free radical nature of the reaction. Several years ago, Dr. Chapiro compiled the work of many investigations of this monomer, from all around the world, and these are shown in Figure 4.⁽¹⁶⁾ What can happen when very pure, very dry styrene is irradiated is shown in Figure 5. It is obvious that a new and different kinetic behavior can be brought out merely by the expediency of removing all impurities, especially water. The rate of polymerization increases by several orders of magnitude and, at one level of dryness, exhibits a linear dependence on intensity. At a higher level of dryness, the absolute values of the rates are even higher, and the dose rate dependency starts to revert back towards a value of one-half.⁽¹⁷⁾

Figure 4

Figure 5

That this behavior of ultra-pure, ultra-dry styrene is peculiar to the radiation induced polymerization process is shown in Figure 6.⁽¹⁸⁾ Here, using the same sample for both studies, the ultraviolet initiation rate shows a one-half order dependency on the intensity, whereas the gamma ray initiated rate shows a first order dependency on intensity.

In addition, the molecular weight of the polymer formed under the conditions of extreme dryness shows little or no dependency on the intensity of the radiation source.^(17,19) Likewise, the temperature coefficient of both the rate of polymerization and the molecular weight are either zero or, perhaps, small negative numbers.^(17,19) Copolymerization studies of styrene with several other monomers⁽¹⁹⁾ conform to what would be expected of an ionic process.

Very similar results have been found for alpha methyl styrene under conditions of extreme dryness, as reported by several workers.^(12,14, 20) In Figure 7⁽²⁰⁾ are shown data obtained at Brookhaven, which shows the same general trend as that previously shown in styrene. In the case of alpha methyl styrene, a complete reversion to a square-root dependency of rate on dose rate can be achieved at very low water concentrations.

These results on pure, dry monomers, as well as many other studies on solutions at low temperature, in the presence of solid

Figure 6

Figure 7

additives, etc., all point to the fact that ions can and do play a role in the radiation chemistry of vinyl monomers. Basically, one must remove all those substances which will inhibit or stop the ionic polymerization process. One of the most pernicious such substances, by virtue of its omnipresence, is water.

One can then postulate that the relative importance of the possible reacting species--free radicals, cations and anions--can be schematically represented, at least tentatively, as shown in Table IV. (17) The first order dependence of the rate of polymerization on the intensity--indicative of a chain termination step which is unimolecular in the propagating species--can be attributed to the predominance of a single ionic process. As the order dependency decreases, while the absolute rate increases, it appears that a second ionic propagation is making its appearance, opening the possibility of both bi-ionic propagation and some amount of cross (bimolecular) termination.

Thus, the study of the radiation induced polymerization of pure liquid vinyl monomers has established the conditions for observing ionic processes in the radiation chemistry of organic compounds and has restored respectability to the name of ionizing radiations.

Table IV

Probable Relative Importance of Active Species in the
Radiation Polymerization of Liquid Styrene
Under Different Conditions of Dryness

Relative Water Content	Relative Over-all Rate of Polymerization	Dose Rate Dependence of Rate of Polymerization (n)	Kinetic Scheme	
			Propagating Species	Termination
High	Low	$n = 1/2$	$R^\bullet$	$R^\bullet + R^\bullet \rightarrow \text{Prod}$
Low	High	$n \approx 1$	$R^+ (>> R^\bullet)$	$R^+ + ? \rightarrow \text{Prod}$
Very Low	Very High	$1/2 < n < 1$	R^+	$R^+ + ?$
			and R^-	$R^- + ?$
				$R^+ + R^- \rightarrow \text{Prod}$

BIBLIOGRAPHY

1. Hall, K. L., R. O. Bolt and J. G. Carroll, "Radiation Effects on Organic Materials," Edited by R. O. Bolt and J. G. Carroll, Academic Press, New York, 1963, p. 117.
2. Weiss, J. and C. H. Collins, Radiation Research, 28, 1 (1966).
3. Samuel, A. H. and J. L. Magee, J. Chem. Phys., 21, 1080 (1953).
4. Davison, W. H. T., S. H. Pinner and R. Worrall, Chem. Ind. (London), 1957, 1274.
5. Okamura, S., T. Higashimura and S. Futami, Isotopes and Radiation (Japan), 1, 216 (1958).
6. Chapiro, A. and V. Stannett, J. chim. phys. 56, 830 (1959).
7. Worrall, R. and A. Charlesby, Intern. J. Appl. Radiation and Isotopes, 4, 84 (1958).
8. Worrall, R. and S. H. Pinner, J. Polymer Sci., 34, 229 (1959).
9. Collinson, E., F. S. Dainton and H. A. Gillis, J. Phys. Chem., 63, 909 (1959): J. Polymer Sci., 34, 241 (1959).
10. Davison, W. H. T., S. H. Pinner and R. Worrall, Proc. Roy. Soc. (London), A252, 187 (1959).
11. Bates, T. H., J. V. F. Best and T. F. Williams, Nature, 188, 469 (1960).
12. Hirota, K., K. Kuwata and K. Makino, Isotopes and Radiation (Japan), 1, 104 (1958).
13. Hirota, K. and F. Takemura, Bull. Chem. Soc. (Japan), 35, 1037 (1962).
14. Best, J. V. F., T. H. Bates and T. F. Williams, Trans. Faraday Soc., 58, 192 (1962).
15. Baumann, C. G. and D. J. Metz, J. Polymer Sci., 62, S141 (1962).
16. Chapiro, A. "Radiation Chemistry of Polymeric Substances," Interscience Publishers, N. Y., 1962, p. 164.

17. R. C. Potter, R. H. Bretton and D. J. Metz, J. Polymer Sci. (in press).
18. Potter, R. C., C. L. Johnson, D. J. Metz and R. H. Bretton, J. Polymer Sci., A4, 419 (1966).
19. Ueno, K., K. Hayashi and S. Okamura, J. Polymer Sci., B3, 363 (1965).
20. Metz, D. J., Advances in Chemistry Series (in press).