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RADIATION DECOMPOSITION OF PURE ORGANIC COMPOUNDS

Bert M. Tolbert and Richard M. Lemmon

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Radiation Laboratory, Department of Physics,
University of California, Berkeley, California

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ABSTRACT

A review is presented on the changes produced in organic compounds by radiation. In general the systems under consideration are restricted to water-free, air-free irradiations of single compounds. Data are reviewed regarding the types of compounds irradiated, the important G values, and the effects of functional groups on radiation sensitivity.

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* This work was supported in part by the U. S. Atomic Energy Commission.

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INTRODUCTION

The fact that ionizing radiation can cause changes in organic compounds has been known for many years, but it has only been in the last 20-30 years that much work has been done on determining the specific changes in organic compounds produced by nuclear radiation, or equivalent artificially-produced radiation. Indeed, real progress has been made in this field only in the last ten years or so.

This review will attempt to cover only radiation changes of a chemical nature in "pure" organic compounds produced by ionizing radiation.[1] "Changes" is perhaps a better word that decomposition since we wish to deal with a variety of effects observed from irradiation -- among which effects are fusion

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* This work was supported in part by the U. S. Atomic Energy Commission.

(1) Recent bibliographies on this subject include:

1. Frances Sachs, "The Effect of α-, β-, γ- and X-rays on Organic Compounds," Carbide and Carbon Chem. Co., Y-12 Plant Report Y-904 (1952).

2. "Ionizing Radiations, Their Production, Effects and Utilization (With Special Reference to Food and Packing Technology)," Bibliographic Series No. 4, Quartermaster Food and Container Inst., NP-5214 (1954), Chicago, Ill.

(including dimerization and polymerization),[2] molecular fission into many different size fragments, oxidation, reduction, rearrangement, and exchanges.

By the term pure organic compounds, we mean to exclude all solution work, and mixtures of organic compounds. Since about half of the papers that have appeared in recent years have dealt with aqueous solutions, and of the remaining only a few are purely organic chemical studies, we are dealing with a rather specialized subject. Our subject is, however, fundamental to the effect of radiation on organic compounds in aqueous solution. Changes in organic compounds in aqueous solution are the result of at least three processes: the direct effect of radiation on the organic compound to produce new stable molecules; the effect on the organic compound of the species arising from the water itself; and lastly, the interaction of reactive species derived from the organic compound, either with themselves or with water and products derived from the water by radiation. Only the first of these three effects is common to solution radiation chemistry and the data reviewed in this paper. This direct effect is especially important for solution work, as it is an isolation of one of the contributors to the over-all changes observed in the irradiation of solutions.

We have preferred to avoid irradiation studies made with air-saturated compounds, since the effect of oxygen in particular adds but one more complicating variable. Such limitations have not always been possible. It should be realized that, ideally, the radiation changes of pure organic compounds can be determined only by extrapolation to zero radiation time. As soon as a compound is irradiated it will be impure, and the effect of those impurities

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(2) The term "polymer" has been used in this review to mean all of the non-volatile products formed during irradiation -- as useful but not necessarily chemically accurate terminology.

on further irradiation can be potentially very important. Thus Jesse and Sadauskis[3] have found marked changes in the ionization potential of noble gases by α-particles in the presence of trace impurities, and many experimenters have found that decomposition products in radiation studies change with increasing time of irradiation.

The chemical changes in organic compounds described in this review are restricted to thos produced by α, β and γ rays, and similar articially produced radiation, including cyclotron-accelerated protons, deuterons, and helium ions, accelerated electrons above 100 kv, and X-rays. Some pile irradiation data are also presented. Radiation decomposition produced by cathode-discharge electrons and ultraviolet irradiation are not included in this review although there are many data on these subjects that are extremely important to this field; cathode-discharge processes will be briefly discussed in the section on irradiation of gases. Ultraviolet radiation studies provide an excellent theoretical background for the work described in this review, but the products of ultraviolet irradiation are often quite different. In photolysis studies relatively few excited states will be produced, since energy is by resonance absorption of the light quanta. In radiolysis studies one can assume as a first approximation that all non-forbidden excited states will be formed. In addition the concentrations of excited and ionized species are quite different.

For consistency within this review, all data are presented as G values; much of the earlier work has been recalculated and necessary approximations made where possible. The G value for an organic compound is used here to

(3) W. P. Jesse and J. Sadauskis, Phys. Rev. 88, 417 (1952).

define the number of a specified ion, atom, radical, or molecule involved in the radiation process per 100 ev of energy absorbed by a system.

Although ion pair yield (-M/N) is very important in radiation chemistry, particularly in gas reaction as pointed out by Lind,[4] it is rather difficult to interpret such data for solids and liquids, and so it is not used here. One part of this expression, -M, is used to represent the starting material that is permanently altered in the radiation process, and the expression G(-M) is used here to mean the molecules of starting material permanently altered per 100 ev energy absorbed.

Radiation and Matter

At one time it was thought that the radiation decomposition process was very unselective, and that the energetic particles or rays broke molecules apart in a rather haphazard manner. It is now known that this is certainly untrue for gases and liquids. Even solid-state irradiations, where very little is known on the details of molecular forces, appear to be capable of correlation and prediction.

The possible processes involved in the interaction between radiation

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(4) S. C. Lind, "The Chemical Effects of Alpha Particles and Electrons," 2nd Ed., Chem. Cat. Co., New York (1928); S. C. Lind, J. Phys. Chem. 56, 920 (1952).

and matter have recently been reviewed in detail,[5-11] and only as much of this material as is needed to clarify this paper will be reviewed here.

The interaction of beta and alpha particles with matter is fundamentally similar, and the loss of energy in both cases is chiefly by interaction with orbital electrons. Only a small part of the total energy is transferred to any one electron, and further the molecule-atom receives but a small fraction of this transferred energy. In the energy ranges used in the studies covered in this review, and in particular for organic compounds, gamma rays lose most of their energy by the Compton effect, in which process the photon transfers part of its energy to an electron. The gamma rays are thus degraded and scattered. At low energies the most important process is photoelectric absorption. The quantum of radiation is completely absorbed in this process and a bound electron is ejected from the molecule. All of

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(5) Faraday Society, London, "Radiation Chemistry," 1952 (Disc. of the Faraday Soc., No. 12).

(6) J. L. Magee, Ann. Rev. of Nuclear Sci. 3, 171 (1953).

(7) J. L. Magee, J. Phys. Chem. 56, 555 (1952).

(8) A. H. Samuel and J. L. Magee, J. Chem. Phys. 21, 1080 (1953).

(9) "Symposium on Radiobiology," Ed., J. J. Nickson, John Wiley & Sons, New York, 1952.

(10) M. Burton, "Ann. Rev. of Phys. Chem.," G. K. Rollefson, Ed., Vol. I, Ann. Rev., Inc., Stanford, Calif., 1950, p. 117.

(11) F. S. Dainton, Ann. Rept. on Progress Chem. (Chem. Soc. London) 45, 5 (1948).

these processes can produce secondary electrons of many hundred ev energy. For one-Mev gamma rays these scattered electrons have a mean energy of 440 kv.[10]

On a molecular level the energetic radiation can either cause the ejection of an electron from a molecule or produce an excited molecule:

$$M \rightsquigarrow M^{+} + e^{-};$$

$$M \rightsquigarrow M^{*}.$$

The secondary electrons from this impact process will continue to produce more ionized or excited molecules until the energy of the electron is less than the lowest excitation potential of the bombarded molecule, and the region of production of these excitations and ionizations is called a "spur." Some of the electrons react with molecules, probably by resonance absorption to produce negative ions (see Figure 1):

$$e^{-} + M \longrightarrow M^{-}$$

$$e^{-} + M^{+} \longrightarrow M^{*}$$

Most of these electrons, however, are thermalized and react with positive ions to form excited neutral molecules. This entire process is very rapid, probably taking place within a molecular vibrational period, and certainly before any gross movement of molecules can occur.[6,8] The transfer of energy to nuclei can produce atomic displacement by recoil and chemical change but these effects are very small for the systems considered here, and represent less then one part in a thousand of the incident energy absorbed.[12]

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(12) R. L. Platzman, "Symposium on Radiobiology," J. J. Nickson, Ed., John Wiley & Sons, New York, 1952, pp. 97-117.

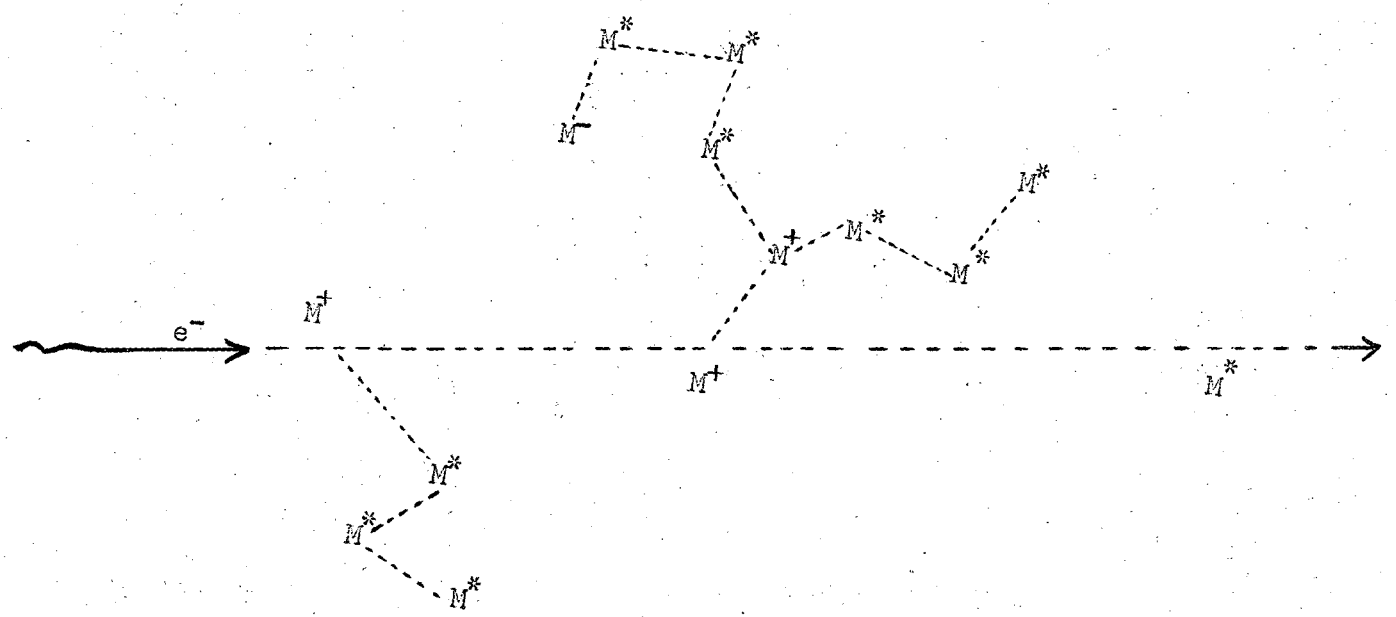

Figure 1

Schematic diagram of a segment of a high-energy electron path.

Chemical Effects

The fate of the excited or ionized molecule determines the chemical effects described in this review. In an ionized molecule the charge apparently assumes a normal probability distribution very rapidly.[13] The excitation energy is converted into vibrational energy, and a fragmentation of the molecule-ion can occur at a point of low transition-state bond energy, which may be quite remote from the point of impact.[14] The ionized molecules may react in other ways, for example, by rearrangement and/or polymerization. The excited molecule can also undergo fragmentation or reaction. Experimental determinations of the number and nature of these activated or ionized intermediates in certain organic compounds have been made by a number of investigators.[15-17]

The fate of the excited or ionized molecule is influenced by the environment; for pure compounds this means whether the radiation is taking place in the gas, liquid, or solid state. The considerable mobility of molecules in gases and liquids should permit the active particles to enter more

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(13) J. Lennard-Jones and G. G. Hall, Trans. Faraday Soc. 48, 581 (1952).

(14) H. Eyring, J. O. Hirschfelder, and H. S. Taylor, J. Chem. Phys. 4, 479 (1936).

(15) L. H. Gevantman and R. R. Williams, J. Phys. Chem. 56, 569 (1952).

(16) A. Prevost-Bernas et al., Disc. of the Faraday Soc. 12, 98 (1952).

(17) W. Minder and A. Heydrich, ibid., 12, 305 (1952).

often into reactions with low transition-state energies than is possible in solids. In addition the fragments produced from the excited or ionized molecule by internal rupture may be greatly influenced by the environment. Therefore, one can expect to find different products from irradiation of a given compound depending on its physical state. Eyring et al.[14] suggest that there is a smaller diversity of products formed in the liquid state than in the gaseous phase.

Effect of Radiation Rate and Type

The effects of varying dose rate and of using different types of radiation, α, β, or γ rays, is usually not predictable. Changes in either of these two variables can produce concentration changes of reactive species, depending upon the time scale. These result in variations in quantity, rather than of type, of chemical products. A number of such examples may be found in the tables. The G(-M) for self-decomposition of C^{14}-labeled organic compounds is usually larger than for γ or e^- irradiations, but in a number of these cases this effect could also be due to other conditions, including purity, temperature, time (compound instability), rate of irradiation, and exposure to oxygen (air) and water.

Irradiation of Gases

The only recent comparative study on the irradiation of gases and liquids is the work of Manion and Burton.[18] Table I shows the results of this study, and there we see that in the gas phase production of hydrogen is greatly depressed and C_2 fragments increased as compared to the liquid state.

Although the relative distribution of positive ions formed by electron

(18) J. P. Manion and M. Burton, J. Phys. Chem. 56, 560 (1952).

Table I

Comparative Irradiation of Gases and Liquids by Electrons

(Manion and Burton)[18]

	Benzene		Cyclohexane	
	Vapor Phase[a]	Liquid Phase	Vapor Phase[a]	Liquid Phase
G (H_2)	0.011	0.036	1.4	5.7
G (CH_4)		0.0012	0.07	0.09
G (C_2 gas)	0.16	0.022	0.48	0.21

(a) The G values for the vapor-phase irradiation may be low by a factor as large as 2.

bombardment can be observed by means of a mass spectrometer, the data so obtained are very difficult to interpret[19] because changes in the accelerating voltage lead to variations in the ratios of the peak intensities of the ions. This situation results from the fact that differing translational energies are imparted to the ions as they are formed, and the greater the translational energy the greater the accelerating voltage needed to cause the ion to reach the collector. Therefore, relative peak heights are not reliable indexes of relative amounts of ions formed. In addition, of course, all neutral fragments are lost in mass spectrometer work. For these reasons attempts such as that of Pahl's[20] to derive an index of radiation stability from mass spectrometer data are of questionable significance.

Wallenstein, Wahrhaftig, Rosenstock, and Eyring[19] have considered the problem of ionizing radiation decomposition of a polyatomic molecule, and find that the calculations are extremely involved and would yield only a general outline of the experimental results. Qualitative considerations of the ionizing-radiation decomposition of a saturated hydrocarbon in a mass spectrometer are listed, and they are consistent with the concept that ionization of the molecule is accompanied by simultaneous transfer of excess energy to other electrons of the molecule, and that a part of this energy is then transferred to the vibrational states of the molecule. Fragmentation can then occur and in a large molecule, such as an octane, a number of stepwise degradations can occur.

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(19) M. Wallenstein, A. L. Wahrhaftig, H. Rosenstock, and Henry Eyring, "Symposium on Radiobiology," Ed. J. J. Nickson, John Wiley & Sons, New York, 1952, p. 70. See also M. Magat and R. Viallard, J. Chim. Phys., 48, 385 (1951).

(20) M. Pahl, Zeit. für Naturfurschung 9b, 188, 418 (1954).

Introduction to Data on Chemical Changes in Organic Compounds

Quantitative data on radiation changes with known radiation energies have been published for about one hundred organic compounds.[21] In the following series of eleven tables we are going to review, by classes of organic compounds, the more important quantitative data for these substances. The accuracy of these reported G values can vary widely. Absolute values of radiation dosage measurements are often in question by one hundred percent. Many of these irradiations have been made without special regard to purity of material, especially oxygen degassing. After irradiation it is often very difficult to remove all of the product gases from an organic solid or liquid, and, therefore, gas G values can be in considerable error unless special precautions are taken.

Of great importance to the specialist in food and drug sterilization are G(-M) and G(polymer)[22] values, and these in particular are lacking in most cases. It is very desirable that more of these values be determined in the future.

Table II summarizes the present status of knowledge on radiation effects for eight types of organic compounds. Compounds that do not undergo known polymerization reactions have G(-M) values varying from 1 to 15. Two notable exceptions are calcium glycolate and choline salts. Production of hydrogen, methane, and other gases are not reliable indexes for molecular stability, even in saturated hydrocarbons. Simple aromatic substances are the most stable class of compounds. Saturated hydrocarbons, halides, alcohols, and aliphatic-α-amino acids are all quite stable.

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(21) The authors regret having neither the time nor space to review the radiation decomposition data of the compounds for which no energy dosage figures are available or calculable.

(22) G(polymer) is calculated as though it were for the reaction G(M $\longrightarrow$ polymer).

Table II

Summation of Radiation Changes in Organic Compounds

	Major G Values Determined
Saturated hydrocarbons	-M,[a] 4 – 9; H_2, 2 – 6; CH_4, 0.06 – 1
Unsaturated aliphatic and alicyclic hydrocarbons	Polymer, 10-2000; crosslink, 6 – 14; H_2, ~1; CH_4, 0.1 – 0.4
Aromatic hydrocarbons	Polymer, ~1; H_2, 0.04 – 0.4; CH_4, 0.001 – 0.08
Halides	1/2 I_2, 2 – 4; HI, 0 1/2 Br, 0 – 0.5; HBr, 0 – 15 1/2 Cl_2, 0; HCl, ~4
Alcohols	-M, 3 – 12; H_2, 1 – 3.5; hydrocarbons, 0.5 – 1.5; carbonyl, 1 – 2; vic-glycol, 0.5 – 1.5
Carboxylic acids	-M, $>$0.3; CO_2, 0.5 – 4; CO, $<$0.5; H_2, 0.5 – 2
α-Amino acids	-M, 3 – 10; NH_3, ~1; CO_2, ~1; amine, ~1
Quaternary ammonium salts	-M, 1 – 170; amine, 1 – 170

(a) The symbol "-M" represents the starting material that is permanently altered.

Saturated Hydrocarbons (See Table III)

Hydrogen gas is one of the major products that has been isolated from irradiation of saturated hydrocarbons. The $G(H_2)$ values gradually decrease with increasing chain length in aliphatic compounds to a value of about 3.5. Extensive branching causes marked deviations from this simple observation.

The $G(CH_4)$ values are increased by the presence of methyl groups. Alicyclic compounds show only trace methane formation, consistent with the idea that most methane is derived from methyl groups. G(-M) values are probably more uniform for this group of compounds than for any others known, and vary from 4-8, which means that while these compounds are not particularly radiation-stable, neither are they subject to chain polymerization reactions induced by radiation.

Unsaturated Aliphatic and Alicyclic Hydrocarbons (See Tables IV and V)

Hydrogen gas production in these compounds is only about one-fourth the amount for the equivalent saturated compounds, i.e., $G(H_2)$ values are about one. Some methane production also is observed. The double or triple bond of unsaturated hydrocarbons does not in itself weaken the molecule with respect to radiation fracture. Indeed such bond energies are 40 to 60 kcal/mole larger than for a simple C-C bond.[23] It may even be that the additional excited energy levels possible in such molecules should result in less fragmentation. However, this effect is obscured by the large amount of starting material that can be polymerized by radiation energy.

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(23) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1942, pp. 53, 131.

Table III

Radiation Changes in Saturated Hydrocarbons

Compound	Radiation	G Values			References
		H_2	CH_4	Others	
Methane	6 Mev α (Rn)	6.5	-	-M,[a] 8.6; ethane, 1.3	24
Ethane	6 Mev α (Rn)	5.0	1.0	-M, 6.6; propane, 0.34	24
Propane	6 Mev α (Rn)	4.26	1.17	-M, 6.6; ethane, 0.68	24
Butane	6 Mev α (Rn)	4.77	0.88	-M, 6.9; ethane, 0.96	24
Cyclohexane	1.5, 0.17 Mv e^-	4.4	0.09	Polymer, 1.7; C_2, 0.21	18,25,26,27
n-Heptane	fast electrons	4.2	0.22	Polymer, 1.7; gas, 4	25,26
n-Hexane	0.17 Mv e^-	4.1	0.33		25
Methylcyclohexane	fast electrons	3.5	-	Gas, 4.5	25,26
n-Decane	0.17 Mv e^-	3.5	0.09		25
n-Tetradecane	0.17 Mv e^-	3.4	0.06		25
2,5-Dimethylhexane	0.17 Mv e^-	2.3	0.62		25
2,2,4-Trimethylpentane	0.17 Mv e^-	1.9	0.82		25
Decahydronaphthalene	0.17 Mv e^-	3.9			25
Polyethylene	γ and n (pile)	-	-	Crosslink, 4	28

(a) The symbol "-M" represents starting material that is permanently altered.

(24) S. C. Lind and D. C. Bardwell, J. Am. Chem. Soc. 48, 2335 (1926).

(25) C. S. Schoepfle and C. H. Fellows, Ind. Eng. Chem. 23, 1396 (1931). Recalculated values using cyclohexane as a standard. Cf. Reference 27 below.

(26) M. Burton, J. Phys. Chem. 52, 564 (1948). Table ascribed to Flanagan, Hochanadel and Panneman.

(27) M. Burton and W. N. Patrick, J. Phys. Chem. 58, 421 (1954).

(28) A. Charlesby, Nucleonics 12, No. 6, 18 (1954).

Table IV

Radiation Changes in Unsaturated Aliphatic and Alicyclic Hydrocarbons

Compound	Radiation	G Values			References
		H_2	CH_4	Others	
Acetylene	6 Mev α (Rn)	0.75	-	Polymer, 75	29
Ethylene	γ rays	-	-	Polyethylene, 10-2000[a]	30
Ethylene	6 Mev α (Rn)	-	-	-M,[b] 20; $H_2 + CH_4$, 3.8	29
Diisobutylene	0.17 Mv e^-	0.87	0.36		25
Octylene	0.17 Mv e^-	1.2	0.09		25
Cyclohexene	1.5, 0.17 Mv e^-	1.2	0.019	C_2, 0.14; polymer, 4.2, 12.4	18,25,26
1-Methylcyclohexene	0.17 Mv e^-	1.1	0.07		25

(a) These values were observed after an induction period which could be due in part to impurities in the ethylene.

(b) The symbol "-M" represents the starting material that is permanently altered.

(29) S. C. Lind, D. C. Bardwell, and J. H. Perry, J. Am. Chem. Soc. 48, 1556 (1926).

(30) J. G. Lewis, J. J. Martin, and L. C. Anderson, Chem. Eng. Progress 50, 249 (1954).

Table V

Polymerization of Unsaturated Aliphatic Hydrocarbons in Pile Irradiation

(A. Charlesby)[31]

Compound	G (Crosslink)	
	cis-stereoisomer	trans-stereoisomer
Decene-1 (C_{10})	10.9	
Octadecene-1 (C_{18})	10.3	
Octadecene-2 (C_{18})	9.2	9.8
Octadecene-3 (C_{18})	7.3	7.7
Octadecene-4 (C_{18})	6.9	7.0
Octadecene-5 (C_{18})	-	-
Octadecene-6 (C_{18})	6.3	6.4
Octadecene-7 (C_{18})	5.9	6.1
Octadecene-8 (C_{18})	6.1	-
Octadecene-9 (C_{18})	6.4	6.1
Decyne-1 (C_{10})	14.3	
Heptadecyne-1 (C_{17})	18.3	
Octadecyne-1 (C_{18})	17.0	
Octacosyne-9 (C_{28})	17.4	
Docosyne-11 (C_{22})	7.1	
Dotriacontyne-16 (C_{32})	8.4	
2,5-Dimethylhexadiene-1,5	13.9	

(31) A. Charlesby, "Effects of Ionizing Radiations on Olefines and Acetylenes," AERE Report M/R-1415, April, 1954.

Several G(polymer) values of 10-75 are listed, and under pressure polyethylene gives a G(polymer) value of 2000 after an induction period that may well be due to trace gas impurities.

In an interesting study on a series of cis- and trans-octadecenes with the double bond in most positions, Charlesby[31] has found crosslink formation is decreased as the double bond is moved away from the end of the molecule, and that the trans-stereoisomer seems to be about 5% more stable than the cis-isomer. This is in agreement with one of Pahl's conclusions[20] from mass spectrometer data that the least stable alkenes are those with the double bond in the one-position.

Aromatic Hydrocarbons (See Table VI)

Simple aromatic hydrocarbons are one of the most stable classes of organic compounds known. The radiation excitation energy can be absorbed in considerable quantity without bond rupture in these molecules, forming triplet states. In the case of benzene, the lowest triplet state has an energy of 3.5 ev.[27,32,33] An excellent protection effect is observed in radiation studies of mixtures of benzene with cyclohexane, and this fact should be remembered in the problems of storage of radiation-sensitive isotopic compounds. However, this protection was not observed for mixtures of propionaldehyde and benzene-d-6, probably because the lowest excited state of the propionaldehyde lies lower than that of benzene. Even polystyrene shows an unusual stability, as measured by physical properties, to pile irradiation,

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(32) W. N. Patrick and M. Burton, J. Phys. Chem. 58, 424 (1954).

(33) S. Gordon and M. Burton, "Radiation Chemistry," Disc. of the Faraday Soc. 12, 88 (1952).

Table VI

Radiation Changes in Aromatic Hydrocarbons

Compound	Radiation	G Values				Reference
		H_2	CH_4	Polymer	Others	
Benzene	1.5 Mv e^-	0.036	0.0012	0.76	C_2, 0.022	18,26,34
Toluene	1.5, 1.8 Mv e^-	0.13	0.008	0.92 1.28	C_2, 0.0043	27,35,36
Ethylbenzene	1.8 Mv e^-	0.18	0.03			35,36
Isopropylbenzene	1.8 Mv e^-	0.17	0.07			36,37
Isopropylbenzene	27 Mev He^{+2}	0.311	0.078		C_2H_6, 0.0054	36,38
tert-Butylbenzene	1.5 Mv e^-	0.11	0.07			36
Mesitylene (1,3,5-trimethyl benzene)	1.8 Mv e^-	0.24	0.018			35
Styrene ($C_6H_5CH{=}CH_2$)	X rays			40 (-18°) 250 (25°) 800 (80°)		39
Polystyrene	γ and n (pile)				Crosslink, 0.08	28

(34) W. N. Patrick and M. Burton, J. Am. Chem. Soc. 76, 2626 (1954).

(35) R. R. Hentz and M. Burton, ibid., 73, 532 (1951).

(36) M. Burton, S. Gordon, and R. R. Hentz, J. Chim. Phys. 48, 190 (1951).

(37) T. J. Sworski, R. R. Hentz, and M. Burton, J. Am. Chem. Soc. 73, 1998 (1951).

(38) A. S. Newton, University of California Radiation Laboratory Report, UCRL-2455 (1954).

(39) D. S. Ballantine, P. Colombs, A. Glines, and B. Manowitz, Chem. Eng. Progress Symposium 50:11, 267 (1954).

presumably because of the protecting benzene ring.[28,40,41] The small amount of hydrogen and methane produced on irradiation of these compounds, in general, increases with increasing number or size of alkyl side groups.

Organic Halides (See Table VII)

The interaction of radiation with organic halides, particularly the iodides and bromides with a small percent of carbon and hydrogen, will certainly be greater with the orbital electrons of the halogen atom itself. However, if charge distribution theories of the primary impact process are correct, this should not be the critical factor, and the molecule should rupture most often at its weakest bond. In an interesting study of free-radical formation in the irradiation of iodides, Gevantman and Williams[15] have shown that in alkyl iodides the C-I bond is more readily broken than the C-C or C-H bonds. However, some C-C bonds are broken, and this type of splitting is more important in the gaseous state of the halides than in the liquid state. The iodine atoms released by this rupture process usually appear in the form of free iodine.

Organic bromides can give either free bromine, HBr, or both; HBr seems to be the more common product. In a study of chloroform irradiation,

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(40) O. Sisman and C. Bopp, U. S. Atomic Energy Commission Unclassified Document, ORNL-928 (1951).

(41) C. Bopp and O. Sisman, U. S. Atomic Energy Commission Unclassified Document, ORNL-1373 (1953).

Table VII

Radiation Changes in Organic Halides

Compound	Radiation	G Values			Reference
		$1/2\ X_2$	HX	Others	
Methyl iodide	1.5 Mv e^-	3.3	-		42
Methyl iodide	X rays 120 p.kv. or 1.3 Mev γ (Co^{60})	2.4	-	H_2, 0.08; CH_4, 0.54; C_2, 1.21	43
Methyl iodide	50 kv β^- (C^{14})	-	-	-M,[a] 3.6	44
Methylene iodide CH_2I_2	1.6 Mv e^-	2.5	-		42
Ethyl iodide	1.6 Mv e^-	4.1	-		42
Ethyl iodide	X rays, 0.96 Å or 4 Å 6 Mev α (Rn) or 5 Mev α (Po)	5.7[b] 2.4[b]	- -		45
Ethyl bromide	1.6 Mv e^- 1.6 Mev X rays	0.2 -	0.6-0.9 2.0[c]		42
Ethylene bromide	1.6 Mv e^- 1.6 Mev X rays	0.5 0.0	- 17.8[c]		42
Ethylene chloride	1.6 Mev X rays	-	4.1[c]		42
n-Propyl iodide	1.6 Mv e^-	2.5	-		42
Bromobenzene	1.6 Mev X rays	-	2.0[c]		42

(a) The symbol "-M" represents the starting material that is permanently altered.

(b) Air-saturated ethyl iodide.

Table VII, Cont.

(c) Yields relative to an assumed $G(1/2\ I_2) = 4.1$ for ethyl iodide decomposition by X-rays.

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(42) R. H. Schuler and W. H. Hamill, J. Am. Chem. Soc. 74, 6171 (1952).

(43) R. C. Petrey and R. H. Schuler, ibid., 75, 3796 (1953).

(44) C. D. Wagner and V. P. Gwinn, ibid., 75, 4861 (1953).

(45) M. Lefort, P. Bonet-Maury and M. Frilley, Compt. Rend. 226, 1904 (1948).

Shulte *et al.*[46] have found no oxidizing agents and only traces of Cl^- formed when specially purified chloroform is irradiated. The C-C bond is probably more readily broken than the C-F bond by radiation, and indeed Teflon shows almost no gas formation on pile irradiation and only crumpling of the polymer to a powder on protracted radiation, presumably due to C-C bond ruptures.[28] When Teflon is irradiated as solid pieces in a sodium hydroxide solution, a certain amount of fluoride is immediately formed, and more slowly appears over the ensuing month. A value of $G(F^-) = 0.54$ was measured for this decomposition by γ-irradiation by Ryan.[47] These data continue the trend observed in the irradiation of iodides and bromides[42] that iodides form iodine, bromides tend to form HBr, and chlorides form no free chlorine. The results on the radiation decomposition of alkyl halides are also in accord with known bond energies: C-F, 107 kcal/mole; C-C, 59 kcal/mole; C-Br, 54 kcal/mole; C-I, 46 kcal/mole.[23] In general, organic halides do not seem to be much more sensitive to radiation changes than are saturated hydrocarbons.

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(46) J. W. Shulte, J. F. Suttle, and R. Wilhelm, J. Am. Chem. Soc. 75, 2222 (1953).

(47) J. W. Ryan, Mod. Plastics 31(2), 152 (1953).

Alcohols (See Table VIII)

In one of the most complete radiation decomposition studies made to date, McDonell and Newton[48] have determined a large fraction of the products produced from He^{+2} bombardment of ten normal-, iso- and tert-aliphatic alcohols. Only a small fraction of the data from this paper is reproduced in the table. Large amoumts of hydrogen are observed in all cases, as are also aliphatic hydrocarbons. Water and carbon monoxide were also formed in all cases. A total of about 7-8 molecular reduction equivalents per 100 ev are formed for each of these compounds.

The principal oxidized products from primary alcohols were aldehydes and glycols; from secondary alcohols, aldehydes, ketones, and glycols; and from tertiary alcohols, ketones with minor amounts of glycols. The products formed indicate that the principal bond rupture occurs at the carbinol carbon atom.

The stability of these alcohols toward radiation changes, as well as that of cholesterol and cholestanol, is normal, and G(-M) values varied from 3.5 — 6.1. Self-radiolysis of methanol-1-C^{14} gave a value of G(-M) = 12. This value is rather high, but this may be due to the difference in radiation.

Amino Acids (See Table IX)

Relatively little data are available on the effects of radiation on pure amino acids, although many such studies have been made with aqueous solutions of these compounds. The available G(-M) values for the pure com-

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(48) W. McDonell and A. S. Newton, J. Am. Chem. Soc., in press.

Radiation Changes in Alcohols

Compound	Radiation	G Values: C_1-C_4 Hydro-carbons	H_2	Carbonyl	vic-Glycol	Reduction Equivalents	-M[a]	Reference
Methyl alcohol	27 Mev He^{+2}	0.40	3.46	1.69	1.75	7.67	5.8[b]	48
Methyl alcohol	50 kv β^- (C^{14})	5.4	5.3	-	1.6	-	12	49
Ethyl alcohol	27 Mev He^{+2}	0.84	3.46	1.10	1.05	8.19	4.73[b]	48
n-Propyl alcohol	27 Mev He^{+2}	1.33	2.80	2.05	0.85	7.30	6.06[b]	48
iso-Propyl alcohol	27 Mev He^{+2}	1.76	2.71	2.96	0.39	8.30	4.73[b]	48
n-Butyl alcohol	27 Mev He^{+2}	1.79	3.59	1.52	0.92	8.53	4.18[b]	48
iso-Butyl alcohol	27 Mev He^{+2}	1.98	2.77	1.65	0.87	7.47	4.83[b]	48
sec-Butyl alcohol	27 Mev He^{+2}	2.22	2.61	2.95	0.56	8.33	6.06[b]	48
tert-Butyl alcohol	27 Mev He^{+2}	2.64	1.24	2.78	0.10	6.97	4.11[b]	48
n-Octyl alcohol	27 Mev He^{+2}	0.03	3.48	0.87	0.56	7.10	-	48
n-Decyl alcohol	27 Mev He^{+2}	0.04	3.47	0.76	0.51	7.14	-	48
Cholesterol	2-4 Mv e^-						3.5	50,[c] 51
Cholesterol	1.3 Mev γ (Co^{60})						3.7	51
Cholestanol	1.3 Mev γ (Co^{60})						4.6	51

(a) The symbol "-M" represents the starting material that is permanently altered.

Table VIII, Cont.

(b) Calculated from authors' data as a minimum value.

(c) The G(-M) for this reference is 170 and is now believed to be in serious error.

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(49) W. J. Scraba, J. G. Burr and D. N. Hess, J. Chem. Phys. 21, 1296 (1953).

(50) B. M. Tolbert, et al., J. Am. Chem. Soc. 75, 1867 (1953).

(51) B. M. Tolbert, R. Noller, and H. Heusser, unpublished data.

Table IX

Radiation Changes of Amino Acids

Compound	Radiation	G Values		Reference
		$-M^a$	Others	
Glycine	2-4 Mv e^-	2.75	CO_2, 0.9; NH_3, 0.73; CH_3NH_2, 1.18; CH_3CO_2H, 0.48; $R(CO_2H)_2$, 0.61	52
Glycine	X-rays	-	NH_3, 9.1	53
Norleucine $C_4H_9CHNH_2CO_2H$	50 kv β^- (C^{14})	9		50
Valine hydrochloride $(CH_3)_2CHCHNH_2CO_2H \cdot HCl$	50 kv β^- (C^{14})	8-16		50
Norvaline hydrochloride $C_3H_7CHNH_2CO_2H \cdot HCl$	50 kv β^- (C^{14})	9		50

(a) The symbol "-M" represents the starting material that is permanently altered.

(52) B. M. Tolbert and R. Noller, Unpublished data.

(53) W. M. Dale, J. V. Davies, and C. Gilbert, Biochem. J. 45, 93 (1949).

pounds are probably not very accurate and, furthermore, are restricted to glycine and three homologues of glycine. Major gas products from irradiation of solid glycine include CO_2, NH_3, and CH_3NH_3. Acetic and oxalic acids are also formed in appreciable quantities. Amine formation from proteins could be partially responsible for off flavors produced in radiation sterilization of high-protein foods.

Carboxylic Acids (See Table X)

The American Petroleum Institute Research Project 43C, located at Massachusetts Institute of Technology, has produced an extensive series of comparative G values on radiation changes in fatty acids under α-particle (Rn) bombardment.[54] Carbon dioxide is the major gas produced. Other gaseous products include CO, H_2O, H_2, and low-molecular-weight hydrocarbons. In a study of temperature effects on hexadecanoic acid (C_{16}, palmitic acid) it was shown that G values for CO_2, CO, and H_2 production increased with increasing temperature. The temperature-vs.-gas production curve for docosanoic acid (C_{22}, behenic acid) was rather anomalous.

In a very recent study, W. M. Garrison et al.[55] and A. S. Newton[56] have shown that dilution of acetic acid with water decreases CO_2, CO, methane, and ethane production proportionally to the added water. This indicates that these products are the result of direct interaction of radiation with acetic acid molecules.

The stability of benzoic acid toward gamma radiation, as measured by decarboxylation and polymer formation, is quite high. This behavior is

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(54) W. L. Whitehead, C. Goodman, and I. A. Breger, J. Chim. Phys. 48, 189 (1951

(55) W. M. Garrison et al., University of California Radiation Laboratory Report, UCRL-2605, May, 1954, p. 28.

(56) A. S. Newton, ibid., p. 28.

Table X

Radiation Changes of Carboxylic Acids

Compound	Radiation	G Values				Reference
		CO_2	CO	H_2	Others	
Acetic acid	27 Mev He^{+2}	4.0	0.4	0.52	C_2H_6, 0.85; CH_4, 1.38	38,56
Acetic acid	6 Mev α (Rn)	2.8	0.5	0.9		54
Benzoic acid	1.3 Mev γ (Co^{60})	0.286	0.0025	0.0026	Polymer, 0.303	52
Octanoic acid (C_8	6 Mev α (Rn)	2.2	0.5	1.4		54
Dodecanoic acid (C_{12})	6 Mev α (Rn)	1.5	0.4	1.5		54
Hexadecanoic acid (C_{16})	6 Mev α (Rn)	1.3	0.3	1.7		54
Eicosanoic acid (C_{20})	6 Mev α (Rn)	0.7	0.2	1.4		54
Docosanoic acid (C_{22})	6 Mev α (Rn)	0.5	0.1	1.2		54
Triacontanoic acid (C_{30})	6 Mev α (Rn)	0.8	0.2	2.3		54
Oleic acid (C_9=C_9)	6 Mev α (Rn)	-	-	-	-M,[a] 2.2	57

(a) The symbol "-M" represents the starting material that is permanently altered.

(57) V. L. Burton, J. Am. Chem. Soc. 71, 4117 (1949).

consistent with the known stabilizing effect of the phenyl group.

Quaternary Ammonium Salts (See Table XI)

The simple quaternary ammonium salt, trimethylethyl ammonium chloride, is quite stable towards both beta and gamma rays and has a G(-M) value of about two. However, the introduction of a β-hydroxyl group into the ethyl radical, giving the biologically-important compound, choline, gives rise to a very radiation-sensitive molecule. Choline chloride has been found to split quite selectively into trimethylamine and acetaldehyde while, at the same time, giving only very small amounts of non-condensable gaseous products. The very high G(-M) values for the self-decomposition of C^{14}-labeled choline chloride and for the γ-irradiated compound are especially striking -- they suggest that a chain reaction must be taking place during the decomposition. The great differences in the G values obtained by the different kinds of radiation is well outside any possible errors of radiation dosage measurements. A time or temperature factor may be involved here, as the γ-irradiation was done over a period of about one week, whereas the 2-4Mev electron bombardments were done in a few minutes.

All of the six systematic changes made in the choline molecule, which are illustrated by the other compounds listed in Table XI, led to increased stability towards radiation, and the G(-M) values obtained need no explanations in terms of chain reactions. The differences between electron and γ-ray bombardment are striking, if real.

Miscellaneous Compounds (See Table XII)

As we have already seen, the radiation stability of organic compounds can vary enormously in a closed system. Gaseous carbon dioxide is one of the most stable compounds observed, probably because of back reaction between the

Table XI

Radiation Changes of Quaternary Ammonium Salts

Compound	Radiation	G Values -M[a,b]	G Values Trimethylamine	Reference
Trimethylethylammonium chloride	1.3 Mev γ (Co^{60})	2	1	58
	2-4 Mv e^-	2	-	58
Choline chloride $[(CH_3)_3NCH_2CH_2OH]Cl$	1.3 Mev γ (Co^{60})	178	171	58
	2-4 Mv e^-	19	21	58
	50 kv β^- (C^{14})	-	490	50,58
Choline iodide $[(CH_3)_3NCH_2CH_2OH]I$	1.3 Mev γ (Co^{60})	7	1	58
	2-4 Mv e^-	4	1	58
Betaine hydrochloride $[(CH_3)_3NCH_2CO_2H]Cl$	1.3 Mev γ (Co^{60})	18	-	58
	2-4 Mv e^-	14	-	58
Trimethyl-2-chloroethylammonium chloride	1.3 Mev γ (Co^{60})	12	12	58
	2-4 Mv e^-	2	6	58
Trimethyl-3-hydroxypropylammonium chloride	1.3 Mev γ (Co^{60})	-	4	58
	2-4 Mv e^-	-	2	58
Acetylcholine chloride $(CH_3)_3NCH_2CH_2OCOCH_3Cl$	1.3 Mev γ (Co^{60})	-	5	58
	2-4 Mv e^-	2	1	58
	50 kv β^- (C^{14})	-	5	58

(a) The symbol "-M" represents the starting material that is permanently altered.

(b) This value determined by Reinecke salt precipitation.

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(58) R. M. Lemmon, M. Parsons, and D. Chin, Abstract of Papers, Division of Organic Chemistry, ACS, September 1954.

Table XII

Radiation Changes in Miscellaneous Organic Compounds

Compound	Radiation	G Values $-M^a$	G Values Others	Reference
Carbon monoxide	6 Mev α (Rn)	6.6		59
Carbon dioxide	6 Mev α (Rn)	0.016		59
Hydrogen cyanide	6 Mev α (Rn)	38.0	N_2, 1.2; H_2, 0.4	29
Cyanogen, C_2N_2	6 Mev α (Rn)	23.4	N_2, 1.0	29
Diisopropyl ether	27 Mev He^{+2}		H_2, 2.3; CH_4, 0.88; C_2, 0.16 C_3, 1.6	38
Dibutyl ether	27 Mev He^{+2}		H_2, 2.7; C_2, 0.16; C_3, 0.25; C_4, 0.38; polymer, 2.5	38
Propionaldehyde	1.5 Mv e^-		H_2, 1.25; CO, 1.60; CH_4, 0.115; C_2, 1.46; C_3, 0.05	32
Methylmethacrylate $CH_2{=}C(CH_3)CO_2CH_3$	X rays		Polymer, 1160 (-18°) Polymer, 3750 (25°) Polymer, 9700 (72°)	39
Calcium glycolate-1-C^{14}	50 kv β^- (C^{14})	166	Oxalic, 61; formic, 105	50,60
Calcium glycolate-2-C^{14}	50 kv β^- (C^{14})	176	Oxalic, 56; formic, 120	50,60

(a) The symbol "-M" represents the starting material that is permanently altered.

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(59) S. C. Lind and D. C. Bardwell, J. Am. Chem. Soc. 47, 2675 (1952).

(60) N. E. Tolbert, Private communication, March 17, 1954.

CO and O formed by the radiation. Mixed gas studies with isotopes could definitely confirm this theory. Methylmethacrylate has a G(polymer) value of 9700 at 72°. The activation energy for this radiation-induced polymerization (4.25 kcal/mole) is very similar to that calculated for photo-initiated free radical polymerizations (4.7 kcal/mole). The anamolous radiation instability of C^{14}-labeled calcium glycolate may be due either to the water of crystallization or to the fact that the compound was not stored *in vacuo*.

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