QUARTERLY REVIEWS

THE ACTION OF IONISING RADIATIONS ON ORGANIC COMPOUNDS

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Introduction

About fifty years have elapsed since the study of radiation chemistry began, and there has been a tendency to regard the subject as primarily the province of the physical chemist. Consequently few investigations have been specifically directed towards the possible use of ionising radiations for synthesis. At the present time we possess a considerable amount of detailed information (albeit incomplete) on the radiation-chemical processes which can occur in one set of systems, namely, aqueous solutions, and a rather unsystematic and often tenuous collection of information on the behaviour of other systems. The ever-increasing availability and cheapness of sources of ionising radiation has caused a new interest in radiation chemistry generally and, in particular, in the possible uses of ionising radiations in organic syntheses. Future developments will undoubtedly include, not only detailed investigations of some simple systems on physicochemical lines, but also a broadening of the scope of the subject by exploration of hitherto untried systems, with the aim of discovering reactions which can most easily be effected by radiation. It is the purpose of this article to summarise what is already known regarding the different types of reaction which can be brought about by ionising radiations, pointing out where possible the principles which lie behind them.

Radiation chemists most commonly employ X- and γ-rays, β-particles, and high-speed electrons, and the densely ionising particles—neutrons, protons, deuterons, and α-particles. Electrical discharges in gases often produce the same effects as radiation, but will not be considered here. The primary action of these radiations on matter is to ionise and excite some of the molecules in the medium irradiated. Both ionised and excited molecules may decompose into free radicals or molecular products, and the subject can, in general, best be understood in terms of the reactions of such radicals and products. Ionising radiations are extremely versatile producers of radicals, being capable of producing them from almost any material in whatever phase, and at any temperature or pH.

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The Primary Act.—As an example of the primary effects which can occur, the action of β-particles on water will be considered. The β-particles eject electrons from water molecules, leaving H_2O^+ ions. The ejected electrons will themselves cause more ionisation and after being slowed down in the process will ultimately, on one commonly accepted picture,[1] be captured by other water molecules to give H_2O^- ions. On the other hand, the β-particles may *excite* some water molecules to a higher electronic level, H_2O^*.

Secondary Processes.—If the ion H_2O^+ is very unstable it may break down before any other process can intervene. One view is that this in fact occurs : [1]

$$H_2O^+ + H_2O \longrightarrow H_3O^+ + \cdot OH$$
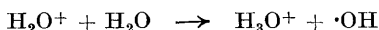
On the other hand the H_2O^+ ion may survive long enough to transfer its charge to a neighbouring molecule, or it might recapture a free electron and give an excited water molecule :

$$H_2O^+ + e \longrightarrow H_2O^\ddagger$$
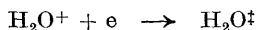
This is another view currently held,[2] the excited state probably being at a higher level than that formed directly.

The H_2O^- ion may also transfer its charge (to a neutral molecule or positive ion) or it may decompose in the following way :
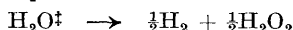
$$H_2O^- \longrightarrow H\cdot + OH^-$$

The second alternative has been widely, though not universally, accepted.

The excited states H_2O^* and $H_2O^\ddagger$ may transfer their excitation energy to neighbouring molecules :

$$H_2O^\ddagger + X \longrightarrow H_2O + X^\ddagger + \text{energy}$$

or they may decompose to radicals or to molecules. One view is that this occurs in the following processes : [2]

$$H_2O^\ddagger \longrightarrow H\cdot + \cdot OH$$
$$H_2O^\ddagger \longrightarrow \tfrac{1}{2}H_2 + \tfrac{1}{2}H_2O_2$$

Whatever the intermediate steps it is generally agreed that the net result may be written [3]

$$H_2O \longrightarrow H\cdot + \cdot OH + H_2 + H_2O_2 + \text{possible other species}$$
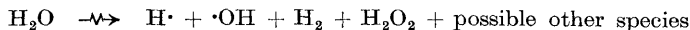
Linear Energy Transfer.—Three important features distinguish radiation chemistry from photochemistry : they are (i) that the energy absorption is non-specific, *i.e.*, energy is absorbed by all components of a system, (ii) that *ions* are formed in the primary act, and (iii) that the absorption of energy, being by collision of *particles* with molecules, tends to be localised along the tracks of the particles and therefore non-uniformly distributed throughout the system. (This applies with equal force to high-energy photon irradiations, as effectively all the energy absorbed by a system so irradiated is

[1] D. E. Lea, " Actions of Radiations on Living Cells ", Cambridge, 1946, p. 47.
[2] A. H. Samuel and J. L. Magee, *J. Chem. Phys.*, 1953, **21**, 1080.
[3] A. O. Allen, *Radiation Res.*, 1954, **1**, 85 ; E. J. Hart, *ibid.*, p. 53 ; H. A. Dewhurst, A. H. Samuel, and J. L. Magee, *ibid.*, p. 62.

ultimately transferred to the system *via* the high-energy electrons ejected during the initial absorption of photons.) The loss of energy per unit path length (linear energy transfer) increases with increasing charge on the particle and with decreasing velocity. Consequently very different values result for, say, electrons and α-particles of the same energy, and the different local concentrations of ions and radicals subsequently set up might be expected to give rise to differences in products and yields for different types of radiation. In aqueous solutions there are many instances of such consequences, but in organic systems there are fewer examples.

Indirect Action.—As an example of indirect action let us consider the irradiation of a dilute aqueous solution. Owing to the non-selective absorption of the energy of ionising radiations and provided there is no marked transfer of energy before the ions and excited molecules of water break down, then the *actual number* of free radicals and other products formed from the water must be greater than the number formed from the solute, very roughly in the ratio by weight of the two substances present. Consequently, as hydroxyl radicals and hydrogen atoms are highly reactive, a solute is far more likely to be affected by these than directly by the radiation. Indirect action of this kind is very common in radiation chemistry.

The Extent of Production of Free Radicals from Organic Substances.—One approach to the determination of the primary effects of radiation on liquids is to use them as solvents and draw conclusions from the changes brought about in solutes at low concentrations. The stable free radical, diphenylpicrylhydrazyl, and various vinyl monomers have been used as solutes, and are assumed to be highly efficient in the trapping of radicals. The extent of the observed reaction is then proportional to the ease of breakdown of the solute by radiation. There are uncertainties in these methods, but there is a fairly good general agreement on the results. The following is the increasing order of radical production for different types of solvent according to the above methods : aromatic hydrocarbons, nitriles, aliphatic hydrocarbons, ethers, alcohols, esters, ketones, and halides.[4] Such methods do not, of course, give any indication of the molecular or ultimate *products* to be expected from irradiations.

Specificity.—It might be expected that the free radicals produced from an irradiated solvent (*e.g.*, hydrogen atoms and hydroxyl radicals from water) would be so reactive that little specificity of attack could occur when a solution of an organic substance is irradiated. However, this does not seem to be the case, and several quite remarkably specific reactions have been discovered.

Similarly, when a pure organic substance is irradiated, it might be supposed that as the energy of the radiation is so great, it would cause fission at the bond at which the " primary act " occurred. Indeed it was earlier suggested that " where special chemical restrictions can be neglected, nature and quantity of the products are determined by nature and number of parent groups in the molecule of the substance decomposed ", this being

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[4] A. Prevot-Bernas, A. Chapiro, C. Cousin, Y. Landler, and M. Magat, *Discuss. Faraday Soc.*, 1952, **12**, 98.

referred to as the " statistical principle ".[5]   However, it has been found that there are more exceptions to the statistical principle than examples of it. This is partly due to the fact that ionisation and excitation energy may be transferred from the site of the primary act to the site at which reaction occurs.   Transfer of ionisation and excitation plays a large part in radiation chemistry, and a further understanding of its mechanism may require advances in theoretical chemistry.   It is a fortunate consequence of its occurrence that the direct action of ionising radiation on an organic compound often gives a quite specific reaction.

Yields.—The yields of radiation-induced reactions can be expressed in two ways.   These are the ionic yield, M/N, and the energy yield, G.   The ionic yield is the number of molecules changed, M, divided by the number, N, of ion pairs formed in the medium.   The energy yield is the number of molecules changed per 100 ev of energy absorbed, and is the more useful concept of the two as it can, in principle at any rate, be measured precisely, whereas in liquids and solids the number of ion pairs formed cannot be measured.

Synthesis

Addition Polymerisation.—Condensed phase.   One of the first radiation-induced polymerisations was Coolidge's irradiation of the leaf of a rubber plant, a white latex being produced.[6]   Since that time it has been amply demonstrated that ionising radiations will initiate the polymerisation of unsaturated compounds.

In the liquid phase, numerous vinyl compounds have been irradiated, both pure and in solution.   They are all polymerised, and in every case the mechanism is a free-radical chain as is shown by the following facts : (*a*) polymerisation can be inhibited by oxygen and benzoquinone and is sensitive to other impurities, although probably not so sensitive as to suggest an ionic mechanism ; (*b*) the molecular weight and the energy yields of the polymers can be very high ; (*c*) the products have in general the usual properties of long-chain polymers produced by free-radical polymerisations ; and (*d*) results of copolymerisation of styrene and methyl methacrylate indicate a monoradical mechanism.[7]   Therefore, in such cases, the situation is one in which the free radicals formed trigger the normal type of vinyl polymerisation.

By far the most usual termination step in free-radical addition polymerisations is that of mutual interaction of the growing chains, leading in the case of a radiation-initiated polymerisation to an expected dependence of the polymerisation rate on the square root of the dose rate.   Such a dependence has been found for styrene,[8, 9] acrylonitrile,[10] and methyl

[5] M. Burton, *J. Chem. Educ.*, 1951, **28**, 404.

[6] W. D. Coolidge, *Science*, 1925, **62**, 441.

[7] W. H. Seitzer, R. H. Goeckerman, and A. V. Tobolsky, *J. Amer. Chem. Soc.*, 1953, **75**, 755.

[8] A. Chapiro, *J. Chim. phys.*, 1950, **47**, 747, 764.

[9] A. Chapiro, M. Magat, J. Sebban, and P. Wahl, Internat. Symposium on Macromolecular Chemistry, Milan, 1954.

[10] A. Prévot, *Comp. rend.*, 1950, **230**, 288.

methacrylate,[11] and for aqueous solutions of acrylamide.[12]   On the other hand, there are also examples of deviations from this dose-rate dependence.[9, 13-15]   Among the possible reasons for this are the perturbing effect of inhomogeneous polymer–solvent system, the co-existence of two types of polymer chain termination,[14] and a transition from termination by mutual interaction of growing chains to termination by initiating radicals as the dose rate is increased.[9]   No one reason has been finally established, but the suggestion has also been made that the deviation may be a specifically radiation-chemical phenomenon, due to the non-uniformity of distribution of the initiating radicals.   No really conclusive comparison as between, say, high-energy β-rays and α-rays has yet been made on any system, but with acrylonitrile in aqueous solution there was no indication of a difference in mechanism with γ-rays, 220-kvp X-rays, 50-kvp X-rays,[13] and 1-Mv electrons.[16]

Of particular interest are the radiation-induced polymerisation of acrylamide in the solid state,[17] and the polymerisation of tetraethylene glycol dimethacrylate at a temperature of $-55°$, probably the lowest temperature at which a free-radical polymerisation has yet been carried out.[18]   Most ethylenic monomers can be polymerised by the action of ionising radiation, but there are three examples of monomers, perfluoropropene, perfluorobutene, and perfluoroacrylonitrile, which have not so far been polymerised in any other way.[19]   Apart from such special cases as those mentioned here, radiation provides a very useful and convenient method of initiating polymerisations under any given conditions and in addition offers the advantage of comparatively easy control of the chain length.

Many polymers can be cross-linked by radiation (see p. 320), although the chemical reactions involved are not always clearly understood.   However, it is noteworthy that those polymers which contain residual unsaturation (e.g., unvulcanised rubber, neoprene) are particularly liable to cross-linking, and the mechanism must be akin to the addition polymerisation discussed here.

Gas phase.   The polymerisation of acetylene by ionising radiations was first investigated in 1925,[6, 20] but it had been known even earlier that electric

[11] A. Chapiro and E. Migirdicyan, *J. Chim. phys.*, 1955, **52**, 439.

[12] R. Schulz, G. Renner, A. Henglein, and W. Kern, *Makromol. Chem.*, 1954, **12**, 20 ;   E. Collinson, F. S. Dainton, and G. S. McNaughton, 5th Meeting of the Société de Chimie physique, Paris, 1955.

[13] E. Collinson and F. S. Dainton, *Discuss. Faraday Soc.*, 1952, **12**, 251.

[14] I. A. Berstein, E. C. Farmer, W. G. Rothschild, and F. F. Spalding, *J. Chem. Phys.*, 1953, **21**, 1303.

[15] B. Manowitz, R. V. Horrigan, and R. H. Bretton, U.S. Atomic Energy Commission Report, 1951, BNL–141.

[16] E. Collinson, unpublished work.

[17] R. B. Mesrobian, P. Ander, D. S. Ballantine, and G. J. Dienes, *J. Chem. Phys.*, 1954, **22**, 565.

[18] J. V. Schmitz and E. J. Lawton, *Science*, 1951, **113**, 718.

[19] B. Manowitz, *Nucleonics*, 1953, **11**, No. 10, 18.

[20] W. Mund and W. Koch, *Bull. Soc. chim. belges*, 1925, **34**, 117.

discharges would bring about the same effect.   Acetylene gas exposed to the action of α-, β-, or γ-radiation yields a yellow solid which absorbs oxygen and resembles cuprene.[21]   A second major product is benzene, which accounts for 15—20% of the total reacting acetylene.[22, 23]   A small amount of hydrogen is evolved which arises mainly from secondary action on the polymer.

The mechanism of the reaction is by no means certain.   The original suggestion was that a " cluster " mechanism operated.   Reactant molecules were supposed to cluster round the primarily formed ions, and on neutralisation they were considered to react to give the final product.[21]   Such mechanisms have lost favour since Eyring, Hirschfelder, and Taylor [24] showed the importance of excited states and free radicals in radiation chemistry, but in this particular case neither a free-radical nor an ionic-chain mechanism seems satisfactory.   Thus, the rate of polymerisation is proportional to the dose rate over appreciable changes of pressure, dose rate, and partial pressure of added inert gas, all of which is difficult to explain on any chain mechanism. Moreover, unlike the situation in photochemical polymerisation, change of temperature has little effect, and the reaction is very reproducible and not prone to inhibition, behaviour very untypical of chain reactions in general and of ionic chains in particular.   On the whole, the reaction seems to be primarily ionic, although recently evidence has been adduced that there may be two concurrent mechanisms.[25]   Further light might possibly be thrown on this problem by measurements of the molecular weights of the polymers, but unfortunately they were insoluble in the limited range of solvents tried.

The irradiation of ethylene is of interest as a practical method of preparing polyethylene without recourse to the high temperature and pressures otherwise required.   When the polymer is prepared by the action of γ-rays at room temperature and at pressures of 20 and 2000 atmospheres,[23, 26, 27] it has much the same properties as the thermal product.   Increase of temperature and dose rate, and decrease of pressure, tend to shorten the chain length.   Not a great deal can be said about the mechanism of the reaction, but it is probably a chain reaction as the energy yields are very high $[- G_\gamma(C_2H_4) \sim 100\text{—}12{,}000$ depending on the conditions].   On the other hand the product of α-irradiation at room temperature and atmospheric pressure is a colourless liquid and an appreciable amount of gaseous product is evolved.[20, 28]   The yield is low $[- G_\alpha(C_2H_4) \sim 18]$ and the reaction is more accurately classed as a condensation.

[21] S. C. Lind, " The Chemical Effects of Alpha Particles and Electrons ", 2nd ed., The Chemical Catalogue Co. Inc., New York, 1928.

[22] C. Rosenblum, *J. Phys. Chem.*, 1948, **52**, 474.

[23] R. H. Bretton, J. C. Hayward, and K. A. Shair, U.S. Atomic Energy Commission Report, 1952, NYO-3309.

[24] H. Eyring, J. O. Hirschfelder, and H. S. Taylor, *J. Chem. Phys.*, 1936, **4**, 570.

[25] R. H. Bretton, J. C. Hayward, and K. A. Shair, U.S. Atomic Energy Commission Report, 1953, NYO-3312.

[26] *Idem, ibid.*, 1952, NYO-3310, 3311.

[27] L. Seed, Atomic Energy Research Establishment Report, 1953, AERE-C/R 1231.

[28] S. C. Lind, D. C. Bardwell, and J. H. Perry, *J. Amer. Chem. Soc.*, 1926, **48**, 1556.

Condensation Polymerisation.—Hydrocarbons. In the previous section we have been discussing an almost exclusively synthetic reaction. In the radiation chemistry of saturated aliphatic hydrocarbons the principal reaction is condensation polymerisation, but some degradation occurs at the same time. This is a natural consequence of the combination and disproportionation of the free radicals and ions initially formed.

In the case of methane, the carbon–hydrogen bond breaks on irradiation, and the fragments react to give ethane and hydrogen : [21]

$$2CH_4 \longrightarrow C_2H_6 + H_2$$
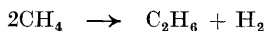
Thus, the irradiation of methane provides an elementary example of condensation polymerisation. However, when higher hydrocarbons are irradiated, although the principal effect is still the fission of carbon–hydrogen bonds, there is also an appreciable amount of fission of carbon–carbon bonds. All the carbon–hydrogen bonds are approximately equally liable to fission and the same is true of all the carbon–carbon bonds.[29] The higher degree of C–H than of C–C breakage is unexpected in view of the higher bond strength of the carbon–hydrogen bond. Attempts have been made to ascribe the phenomenon to a cage effect.[30] The hydrogen atom liberated by carbon–hydrogen fission is considered to be easily removed by diffusion, whereas when a carbon–carbon bond is broken, the larger fragments cannot so easily escape, and so tend to recombine. However, such explanations cannot explain the results in the gas phase. It seems rather that the phenomenon is a specifically radiation-chemical one, for which we cannot yet give an explanation.

From what has been said above it is apparent that radiation does not simply produce the same " cracking " of hydrocarbons as is produced by heat. The products are found to include hydrogen and hydrocarbons of lower molecular weight than the original, but also hydrocarbons of higher molecular weight which are partly cross-linked and partly unsaturated. The hydrocarbons of lower molecular weight contain very little unsaturated product.[21, 31]

For a hydrocarbon containing both single and double bonds the statistical principle might lead one to expect that the ratio of attack at the saturated part of the molecule to attack at the unsaturated part could be proportional to the ratio of the amounts of each. This is found not to be the case. When polyethylene is irradiated the vinylidene groups decrease more rapidly than expected, so that migration of chemical reactivity must be occurring, causing a degree of specificity of attack at these positions.[32] Whether the migration is of energy or of free-radical centre is as yet undecided.

It is of interest that the production of cross-linking in hydrocarbons, polyethylene, and other substances leads to marked changes in their physical properties, *e.g.*, the melting point increases and the product becomes

[29] A. Charlesby, *Proc. Roy. Soc.*, 1954, *A*, **222,** 60.
[30] M. Burton, *J. Phys. Colloid Chem.*, 1947, **51,** 611.
[31] R. E. Honig and C. W. Sheppard, *J. Phys. Chem.*, 1946, **50,** 119.
[32] M, Dole, C. D, Keeling, and D. G. Rose, *J. Amer. Chem. Soc.*, 1954, **76,** 4304.

insoluble in normal organic solvents. Such changes may prove to be of technical importance.[33]

Glycol formation from alcohols. A marked specificity of attack is observed when alcohols are irradiated.[34] The bonds linking the carbinol-carbon atom to groups other than the hydroxyl group are preferentially broken, probably owing to their being weakened by polarisation induced in them by the hydroxyl group. In primary and secondary alcohols it is the carbon–hydrogen bond which breaks. The atoms and radicals produced by fission then unite to give *vic.*-glycols and hydrogen, the overall reaction being of the type :

$$2CH_3 \cdot CH_2 \cdot OH \;\longrightarrow\; \begin{array}{c} CH_3 \cdot CH \cdot OH \\ | \\ CH_3 \cdot CH \cdot OH \end{array} + H_2$$
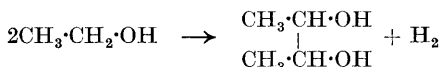
At the same time there can be further oxidation of the free hydroxyethyl radicals ; so that primary alcohols also give aldehydes, and secondary alcohols give ketones. It is worthy of note that whereas α-particles were found to produce these further oxidations, β-particles acted on methanol to give simply ethylene glycol and hydrogen with no formaldehyde.[35] *tert.*-Butyl alcohol, the only tertiary alcohol so far irradiated, did not give any glycol, but only ketone.

Dimerisations in aqueous solution. Dimerisations are frequently observed when organic substances are irradiated in aqueous solution. Thus, primary alcohols give glycols,[36] formic acid gives oxalic acid,[37] acetic acid gives succinic acid,[38] and benzene gives diphenyl.[39] Such reactions are always accompanied by other, often quantitatively more important reactions, but by adjusting the conditions it is sometimes possible to favour one reaction rather than another. For example, aqueous benzene gives more phenol than diphenyl when irradiated in the presence of dissolved oxygen, but when dissolved hydrogen is present instead the oxidation reaction is partly suppressed and diphenyl is the principal product. This is probably partly due to the removal of hydroxyl radicals by the process,

$$\cdot OH + H_2 \longrightarrow H_2O + H\cdot.$$
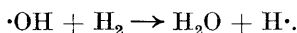
Degradation

Decarboxylation.—We have already seen that the presence of a double bond or alcohol group in a saturated aliphatic compound causes marked specificity of behaviour in irradiation. Several other groups, of which the carboxyl group is one, also produce specific effects. Irradiation of carboxylic

[33] A. Charlesby, *Nucleonics*, 1954, **12**, No. 6, 18.

[34] W. R. McDonell and A. S. Newton, *J. Amer. Chem. Soc.*, 1954, **76**, 4651.

[35] W. J. Skraba, J. G. Burr, and D. N. Hess, *J. Chem. Phys.*, 1953, **21**, 1296.
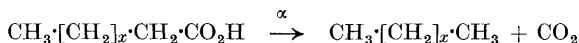
[36] G. Scholes, 5th Meeting of the Société de Chimie physique, Paris, 1955 ; W. R. McDonell, *J. Chem. Phys.*, 1955, **23**, 208.

[37] W. M. Garrison, D. C. Morrison, H. R. Haymond, and J. G. Hamilton, *J. Amer. Chem. Soc.*, 1952, **74**, 4216.
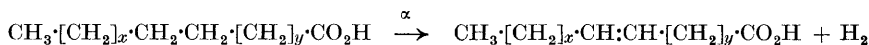
[38] W. M. Garrison, H. R. Haymond, D. C. Morrison, B. M. Weeks, and J. Gile-Melchert, *J. Amer. Chem. Soc.*, 1953, **75**, 2459.

[39] G. Stein and J. Weiss, *J.*, 1949, 3245.

acids gives rise to both dehydrogenation and decarboxylation, but not both in the same molecule ; [40, 41] *e.g.* :

$$CH_3 \cdot [CH_2]_x \cdot CH_2 \cdot CO_2H \xrightarrow{\alpha} CH_3 \cdot [CH_2]_x \cdot CH_3 + CO_2$$

and

$$CH_3 \cdot [CH_2]_x \cdot CH_2 \cdot CH_2 \cdot [CH_2]_y \cdot CO_2H \xrightarrow{\alpha} CH_3 \cdot [CH_2]_x \cdot CH:CH \cdot [CH_2]_y \cdot CO_2H + H_2$$
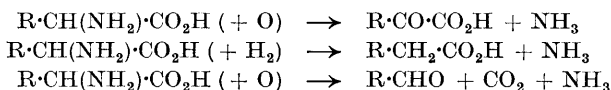
The proportion of decarboxylation to dehydrogenation varies in a complex manner with the size of the irradiated molecule in going from acetic to melissic acid (C_{30}) but no explanation is yet available.

It has been suggested that the decarboxylation of aliphatic acids by radiation may explain how hydrocarbons are formed in Nature. One of the difficulties of the theory is the fact that dehydrogenation always occurs simultaneously with decarboxylation, and yet hydrogen is not found in oil fields. A possible reason might be that under the influence of radiation the hydrogen is used to saturate double bonds. This reaction does not take place on irradiation of mixtures of hydrogen with simple hydrocarbons such as ethylene, but it seems to be possible when oleic acid is irradiated, some stearic acid being formed.[42] The irradiation of oleic acid is interesting from another point of view, in that the heptadec-8-ene which is one of the main products is present in a particularly pure form. It has been suggested that radiation-decarboxylation might be better than any other existing method of preparing such compounds.

It may be useful from a synthetic viewpoint that salts and esters appear to be less readily decarboxylated than acids themselves. In these cases dehydrogenation is the predominant reaction. It is noteworthy that the only aromatic acid irradiated, benzoic acid, suffered only little decarboxylation and even less dehydrogenation. Resistance to decomposition by the direct action of ionising radiations is a characteristic of aromatic compounds. Possible reasons are given later (p. 321).

Deamination.—Most of the work on deamination has been with aqueous solutions of amino-acids [43] and other compounds containing amino-groups,[44] the stimulus for such studies arising from the interest in the biological effects of ionising radiations. Alanine and glycine have been shown to be deaminated in air-free solution by three principal reactions ; [45] in decreasing order of importance they are :

$$R \cdot CH(NH_2) \cdot CO_2H \; (+ O) \longrightarrow R \cdot CO \cdot CO_2H + NH_3$$
$$R \cdot CH(NH_2) \cdot CO_2H \; (+ H_2) \longrightarrow R \cdot CH_2 \cdot CO_2H + NH_3$$
$$R \cdot CH(NH_2) \cdot CO_2H \; (+ O) \longrightarrow R \cdot CHO + CO_2 + NH_3$$

[40] C. W. Sheppard and V. L. Burton, *J. Amer. Chem. Soc.*, 1946, **68,** 1636.

[41] W. L. Whitehead, L. Goodman, and I. A. Breger, *J. Chim. phys.*, 1951, **48,** 184.

[42] V. L. Burton and I. A. Breger, *Science*, 1952, **116,** 477.

[43] W. M. Dale, *J. Cell. Comp. Physiol.*, 1952, **39,** Suppl. 1, p. 39 ; G. Stein and J. Weiss, *J.*, 1949, 3256.

[44] G. Scholes and J. Weiss, *Biochem. J.*, 1953, **53,** 567.

[45] C. R. Maxwell, D. C. Petersen, and N. E. Sharpless, *Radiation Res.*, 1954, **1,** 530 ; N. E. Sharpless, A. E. Blair, and C. R. Maxwell, *ibid.*, 1955, **2,** 135.

The principal effect of deuterons on glycine in the dry state has been shown to be decarboxylation rather than deamination.[46]

Degradation and Synthesis of Macromolecules.—Many materials of high molecular weight are degraded on irradiation, whilst others exhibit an increase in molecular weight.

Synthetic polymers. The effects of radiation on a very large number of polymers have now been investigated.[33] The effect on straight-chain polymers of vinyl type, in the absence of oxygen, appears to be predictable from their structure,[47] but the explanation of the generalisations is harder to find. Supposing the polymer to be of the form $[-CH_2 \cdot CR^1R^2-]_n$, cross-linking will result if R^1 or R^2, or both, are hydrogen atoms. If R^1 and R^2 are organic groups irradiation will cause degradation, and the efficiency and type of degradation will be determined by the nature of R^1 and R^2. Degradation may occur in the main chain or in the groups R^1 and R^2, but in no case yet examined has degradation resulted in monomer production.

In agreement with the above generalisations poly(methyl methacrylate) ($R^1 = Me$, $R^2 = CO_2Me$) suffers degradation in the main chain and in the ester group.[48] Polyethylene ($R^1 = H$, $R^2 = H$ or a branch), as already noted, is predominantly cross-linked with little fission of the main chain,[32, 49] but another effect enters here, namely, the increased tendency to cross-linking when residual unsaturation is present, owing to localisation of chemical activation at the unsaturation. Poly*iso*butene. ($R^1 = R^2 = Me$) suffers rapid degradation of the main chain.[50] Possible factors here are that the methyl groups assist degradation by causing strain in the molecule and by favouring intramolecular cross-linking.

The behaviour of poly(vinyl chloride) and poly(vinylidene chloride) is exceptional in that, in addition to the expected cross-linking, elimination of hydrogen chloride occurs.[51]

Irradiation in the presence of oxygen gives very different effects, oxidation being predominant.

Another way in which degradation of polymers can be brought about is by irradiation in solution. In such cases the effect is one of indirect action. The presence of oxygen is necessary for degradation to occur, and it has been suggested that poly(methacrylic acid) is only degraded by the HO_2 radical.[52] However, this cannot be formed in some of the organic solvents and consequently a mechanism involving organic peroxides seems to be more likely.[53]

Other large molecules. Irradiation of nucleic acids in aqueous solution causes molecular breakdown which can be followed by the resultant decrease in viscosity. The action is an indirect one and probably involves a complex

[46] I. A. Breger, *J. Phys. Colloid Chem.*, 1948, **52**, 551.

[47] A. A. Miller, E. J. Lawton, and J. S. Balwit, *J. Polymer Sci.*, 1954, **14**, 503.

[48] P. Alexander, A. Charlesby, and M. Ross, *Proc. Roy. Soc.*, 1954, A, **223**, 392.

[49] A. Charlesby and N. H. Hancock, *ibid.*, 1953, A, **218**, 245.

[50] E. J. Lawton, A. M. Bueche, and J. S. Balwit, *Nature*, 1953, **172**, 76.

[51] E. J. Henley and A. Miller, *Nucleonics*, 1951, **9**, No. 6, 62.

[52] P. Alexander and M. Fox, *Trans. Faraday Soc.*, 1954, **50**, 605.

[53] L. A. Wall and M. Magat, *J. Chim. phys.*, 1953, **50**, 308.

sequence of reactions.[44]   Polysaccharides are also degraded, whilst proteins are cross-linked.

Radiation-resistance of Aromatic Compounds.—An outstanding property of aromatic hydrocarbons is their relatively high resistance to decomposition by ionising radiations, compared with corresponding aliphatic compounds. This effect is very marked with respect to gaseous products, but it is not so significant when polymer yields are also taken into account.   For example, the rate of decomposition of benzene vapour to gaseous products is one-eighth of that of *cyclo*hexane under the same conditions of irradiation,[54] but the yield of polymer from benzene is greater than that from *cyclo*hexane, bringing the total decomposition yield of benzene to about half that of *cyclo*hexane. However, the effect of state is more marked for aromatic compounds than for aliphatic compounds, and in the liquid state both the gas and the polymer yield are less for benzene than for *cyclo*hexane, the ratio of total yields being about 1 : 10.[55]

The explanation of the stability of aromatic hydrocarbons has been discussed by M. Burton,[5] who suggests that it arises from the delocalisation of excitation energy in the ions and excited molecules initially produced. It is possible for energy to be transferred from a side chain to a benzene ring, and to be dissipated without reaction.   This effect is termed " sponge-type " protection and explains why compounds containing aromatic groups are less reactive than would be expected on the statistical principle.   The low yield of benzene from benzoic acid has been mentioned already.   Another example is polystyrene, which requires a higher dose of radiation than polyethylene for a given amount of cross-linking and does not undergo carbon–carbon fission at all.[56]   Such protection is not restricted to intramolecular energy transfer, but can also occur intermolecularly in mixtures.   An example is the irradiation of mixtures of *cyclo*hexane and benzene, the *cyclo*hexane being protected by excitation and ionisation transfer to the benzene.[55, 57]   The phenomenon appears to depend on the ionisation and excitation potentials of the components, and for a mixture of propionaldehyde and hexadeuterobenzene, where the lowest excited state of propionaldehyde is lower than that of benzene, there is no protection of the aldehyde.[58]

Oxidation

The Oxidation of Pure Substances by Dehydrogenation.—It will have been noticed from the previous sections that, except for compounds containing reactive double or triple bonds, organic compounds are often dehydrogenated on irradiation.   When the radical fragments react in such a way as to increase the number of carbon atoms in the molecule we have preferred to classify such reactions as condensation polymerisation.   However, two cases, alcohols and carboxylic acids, merit further discussion.

[54] V. P. Henri, C. R. Maxwell, W. C. White, and D. C. Petersen, *J. Phys. Colloid Chem.*, 1952, **56,** 153.

[55] J. P. Manion and M. Burton, *ibid.*, p. 560.

[56] A. Charlesby, *J. Polymer Sci.*, 1953, **11,** 513.

[57] M. Burton and W. N. Patrick, *J. Phys. Chem.*, 1954, **58,** 421.

[58] W. N. Patrick and M. Burton, *ibid.*, p. 424.

We have seen that glycols are formed on irradiation of alcohols. In addition, with α-particles, there is always some further dehydrogenation of the intermediate radical to give carbonyl compounds. The amount of aldehyde or ketone formed on α-particle-irradiation of alcohols is generally comparable with the amount of glycol, but on irradiation of *tert.*-butyl alcohol the principal product is acetone and there is practically no glycol, so that oxidation is the principal reaction in this case.[34]

We have also noted that carboxylic acids and especially their salts and esters are dehydrogenated on irradiation as well as being decarboxylated. The products of dehydrogenation have not been extensively studied, but are probably unsaturated acids.[41] This reaction resembles the production of unsaturation which is one of the reactions which occurs when hydrocarbons are irradiated.

Oxidation in the Presence of Molecular Oxygen.—Oxygen usually has a profound effect on radiation-induced changes, the normal reactions which occur in the absence of oxygen tending to be suppressed in favour of oxidation. The reason may be the readiness with which free-radical intermediates add to molecular oxygen.

The polymerisation of cyanogen provides a particularly striking example of preferred oxidation.[28] In the absence of oxygen a black polymer resembling paracyanogen is formed on irradiation, but with oxygen present, although polymerisation still occurs, it follows a different course, and a yellow solid of composition $(CNO)_n$ is formed instead.

There are also good examples of oxidation in the radiation chemistry of the hydrocarbons. When hydrocarbons are irradiated with α-particles they are dehydrogenated with the formation of both higher and lower hydrocarbons (see p. 317). If however the hydrocarbon is mixed with oxygen, irradiation gives carbon dioxide and water, and the normal dehydrogenation is suppressed.[28] There is complete suppression of the normal reactions of methane and ethane, but in the irradiation of higher hydrocarbons suppression is not complete and both reactions take place simultaneously.

The radiation-oxidation of aliphatic halides and especially of chloroform has received considerable study. According to one school the most important initial stage in the oxidation of chloroform is the formation of a peroxide (probably $CCl_3 \cdot O \cdot OH$) with a yield high enough to be indicative of a chain reaction : [59]

$$CHCl_3 + O_2 \longrightarrow CCl_3 \cdot O \cdot OH$$
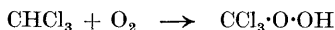
In the next step the peroxide disappears and carbonyl chloride, hydrochloric acid, and other products are formed. The reaction is extremely sensitive to impurities and the agreement between results obtained by different workers is not good.

The radiation-induced oxidation of hydrocarbons and also of fats, like that of chloroform, proceeds through a peroxidic intermediate.[60] Indeed it may well be that peroxides are always produced in radiation-induced oxidations when molecular oxygen is present.

[59] J. W. Schulte, J. F. Suttle, and R. Wilhelm, *J. Amer. Chem. Soc.*, 1953, **75**, 2222.
[60] R. S. Hannan and J. W. Boag, *Nature*, 1952, **169,** 152.

Oxidation in Aqueous Solution.—Hydrogen atoms and hydroxyl radicals are present together in irradiated water, so that both reduction and oxidation are possible when substances are irradiated in aqueous solution. In practice, however, the oxidising power of the hydroxyl radical is such that oxidation is the more usual reaction. Moreover, when dissolved oxygen is present, peroxide radicals can be formed both by hydrogen atoms and by organic free-radical intermediates, so that oxidations tend to be favoured under these conditions.

Alcohols give *vic.*-glycols on irradiation in aqueous solution (see p. 318). However, primary alcohols give aldehydes as well, and when dissolved oxygen is present the yield of aldehyde increases several-fold.[61] It is not yet known whether the yield of glycol shows a corresponding decrease, although this would be expected.

Oxidation of alcohols to carbonyl compounds appears to be a general result of irradiation in aqueous solution, having been observed also with hydroxy-acids [62] and carbohydrates.[63] The extent of oxidation is always increased when dissolved oxygen is present.

The irradiation of aqueous D-mannitol is interesting : [63] D-mannose is formed, showing that with both primary and secondary alcohol groups on the molecule the attack is almost exclusively on the primary group. Similarly D-glucose, D-galactose, and D-mannose give good yields of the corresponding uronic acid. Evidently in these cases the primary alcohol group is oxidised to aldehyde, and the resulting molecule changes to the uronic acid.

It is well known that all oxidising agents will react with thiols, and it is not surprising that the main effect of irradiating aqueous solutions of thiols is to produce oxidation. Thus, cystine is formed on irradiation of aqueous cysteine.[64] The yield is higher when dissolved oxygen is present. The cystine produced is not affected until most of the cysteine has gone, but is ultimately further oxidised, probably to the disulphoxide.[65]

Cysteine is most readily autoxidised in alkaline solution and in line with this it is found that the radiation-induced oxidation increases with pH. The yield also increases with concentration of cysteine. Very high yields are obtained in concentrated solutions, indicating that a chain reaction is taking place.[66]

Another product obtained by irradiating cysteine is hydrogen sulphide, which is formed in about 0·5% of the cystine yield.[67] Deamination which is important for other amino-acids does not occur.

Aromatic compounds are hydroxylated on irradiation in aqueous solution. Work on this reaction was one of the first investigations giving information

[61] A. J. Swallow, *Biochem. J.*, 1953, **54**, 253.

[62] G. R. A. Johnson, G. Scholes, and J. Weiss, *J.*, 1953, 3091 ; A. W. Pratt and F. K. Putney, *Radiation Res.*, 1954, **1**, 234.

[63] G. O. Phillips, *Nature*, 1954, **173**, 1044.

[64] S. L. Whitcher, M. Rotheram, and N. Todd, *Nucleonics*, 1953, **11**, No. 8, 30.

[65] M. Rotheram, N. Todd, and S. L. Whitcher, *Naturwiss.*, 1952, **39**, 450.

[66] A. J. Swallow, *J.*, 1952, 1334.

[67] W. M. Dale and J. V. Davies, *Biochem. J.*, 1951, **48**, 129.

about the free hydrogen atoms and hydroxyl radicals present in irradiated water, and with this object Stein and Weiss have compared the action of radiation with that of Fenton's reagent, which is believed to act by the production of hydroxyl radicals. The detailed mechanism is not the same in both cases but there is a broad parallelism, not only for aromatic substances but also for compounds of many other types.

The effect of irradiating aqueous benzene has already been mentioned. Nitrobenzene, benzoic acid, and chlorobenzene have each been found to be hydroxylated in all three possible positions, and there is also some attack at the functional group.[68] Phenol is hydroxylated more specifically, only o- and p-dihydroxybenzene being formed.[69] Phenol also gives some o-benzoquinone, and this appears to be formed directly rather than by further reaction of the irradiation product.

Oxidation in Non-aqueous Solution.—Irradiations have been made of cholesterol and its derivatives, and of other steroids, when dissolved in various air-saturated organic solvents.[70] The products isolated were relatively few and it seems that attack occurred only at one or more of the positions 3, 5, 6, and 7, and that in each case oxidised products were formed. It is also interesting that certain steroids (cholestane, cholest-3-ene, cholest-5-ene, and cholestan-3-one) were hardly affected by quite large doses of X-rays.

In some cases the steroids were irradiated in acetic acid solution, and acetylated products were produced. This shows that ionising radiations have possibilities in causing reactions other than straightforward oxidation.

Halogenation

Free radicals will react readily with iodine, and by investigating the nature of the iodides formed this property has been used to obtain information about the nature of the radicals produced on irradiating aliphatic hydrocarbons. The reaction could presumably be used as a method of preparative iodination of hydrocarbons and possibly other compounds. It has been found by work with radioactive iodine that hydrocarbons give a mixture of iodides when irradiated in the presence of iodine, and that the iodides always contain either the same or a smaller number of carbon atoms than did the original compound.[71] This result is expected in view of the fact that both carbon–hydrogen and carbon–carbon bonds are broken when hydrocarbons are irradiated.

An early example of chlorination by radiation was Alyea and Lind's demonstration that α-particles, like light, will induce the synthesis of carbonyl chloride from carbon monoxide and chlorine.[72] The yield was

[68] H. Loebl, G. Stein, and J. Weiss, *J.*, 1950, 2704 ; *J.*, 1951, 405 ; G. R. A. Johnson, G. Stein, and J. Weiss, *J.*, 1951, 3275.

[69] G. Stein and J. Weiss, *J.*, 1951, 3265.

[70] M. Keller and J. Weiss, *J.*, 1950, 2709 ; B. Coleby, M. Keller, and J. Weiss, *J.*, 1954, 66.

[71] R. R. Williams and W. H. Hamill, *J. Amer. Chem. Soc.*, 1950, **72,** 1857 ; L. H. Gevantman and R. R. Williams, *J. Phys. Chem.*, 1952, **56,** 569.

[72] H. N. Alyea and S. C. Lind, *J. Amer. Chem. Soc.*, 1930, **52,** 1853.

very high and the reaction must have been a chain reaction. Aromatic hydrocarbons can also be chlorinated *via* a chain reaction,[73] and when mixtures of chlorine and benzene were irradiated with γ-rays, good yields of 1 : 2 : 3 : 4 : 5 : 6-hexachloro*cyclo*hexane were obtained.

The chlorination of toluene is interesting in that γ-radiation causes addition to the nucleus as well as substitution in the side-chain. This result is unexpected as it is well known that ultraviolet light leads only to side-chain substitution. It seems that not only the primary act but also the subsequent reaction mechanism differs in the two cases.

Reduction

Mixtures with Hydrogen in the Gas Phase.—Though hydrocarbons cannot be hydrogenated by the irradiation of mixtures with hydrogen, other reductions can be achieved in this manner. It has been known since 1913 that under the influence of α-radiation carbon dioxide and hydrogen give formaldehyde, which then reacts further. Carbon monoxide can be reduced similarly. The final product of irradiation in both cases is a white solid of composition $(CH_2O)_n$ which is presumably produced by polymerisation of the formaldehyde.[74] Oxygen inhibits the reaction.[75]

Reduction in Oxygen-free Aqueous Solution.—*Reversible oxidation–reduction systems.* Two reactions can take place when the dyes used as oxidation–reduction indicators are irradiated in oxygen-free aqueous solutions : the oxidised form of the dye can be reversibly reduced, presumably by hydrogen atoms, to the normal reduced form of the dye ; or both oxidised and reduced forms can be irreversibly oxidised by hydroxyl radicals to unknown products. The normal reversible oxidation of the *leuco*-dye does not in general take place.

The existence of these two reactions, reversible reduction and irreversible oxidation, is exemplified in work by Seitz,[76] who showed that air-free aqueous solutions of a wide range of dyes are decolorised by X-rays. Oxygen was introduced at the end of the irradiations, and much of the colour was restored, proving that the *leuco*-dye had been formed. Restoration of the colour was not complete, however, owing to the formation of the irreversibly oxidised form. This interpretation has been established in the case of methylene-blue by direct spectrophotometric observation of the simultaneous formation of the *leuco*-dye and an irreversibly oxidised product in air-free aqueous solutions subjected to X-irradiation.[77]

It is possible to suppress the oxidising action of the hydroxyl radicals, and ensure complete reduction, by adding an excess of a substance which reacts with hydroxyl radicals, for example, sodium benzoate.[78] The effect

[73] D. E. Harmer, J. S. Martin, and L. C. Anderson, 5th Meeting of the Société de Chimie physique, Paris, 1955.

[74] S. C. Lind and D. C. Bardwell, *J. Amer. Chem. Soc.*, 1925, **47**, 2675.

[75] S. C. Lind and P. S. Rudolph, Abs. Amer. Chem. Soc. symposium, March—April, 1954, p. 9Q.

[76] W. Seitz, *Strahlentherapie*, 1938, **61**, 140.

[77] E. Collinson, *Discuss. Faraday Soc.*, 1952, **12**, 285.

[78] M. J. Day and G. Stein, *Nature*, 1950, **166**, 146.

of such a substance may be two-fold, for it can only remove hydroxyl radicals by replacing them with other radicals and these in favourable cases may be reducing agents. A useful substance to add is carbon monoxide, for after irradiation the excess of carbon monoxide and the dioxide formed can easily be removed from the solution.[16] This may prove a useful method for preparing pure solutions of *leuco*-dyes.

In one case, diphosphopyridine nucleotide, reduction is impossible except when certain added substances, *e.g.*, ethanol. are present.[61, 79] The explanation offered is that hydrogen atoms cannot reduce this substance, but that certain organic free radicals, such as the hydroxyethyl radical, can. It is of interest that the reduced form obtained is not identical with the form produced by reduction with enzymes or with sodium dithionite, but appears to resemble one of the reduction products obtained by the action of sodium borohydride.

Steroids. Irradiation of air-free aqueous solutions of cortisone and deoxycorticosterone leads to dehydroxylation in the 17α- or the 21-position of cortisone, and correspondingly in the 21-position of deoxycorticosterone.[80]
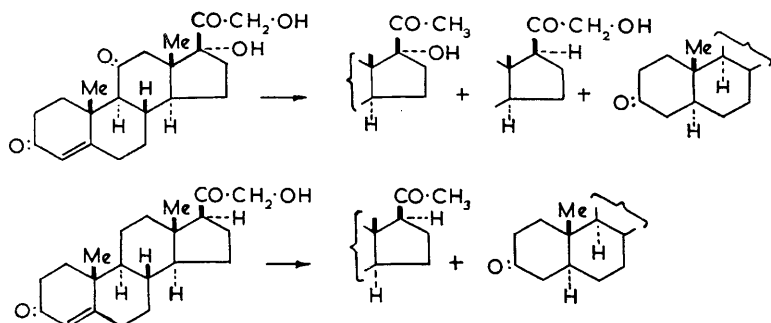
There is also hydrogenation of the double bond. These results contrast with the result of irradiating air-saturated solutions of sterols in organic solvents.

Reduction in Alcoholic Solution.—Both the mass spectrometry of alcohols and the nature of the final products of irradiation indicate that alcohols give hydroxyalkyl radicals and hydrogen atoms on irradiation. Both are probably reducing agents and it might be expected that reduction would be common in alcoholic solutions, provided that oxygen is absent. There has been little work in this field, but Piffault, Blanquet, and Duhamel[81] have noted that glycerol solutions of methylene-blue were reversibly decolorised by *X*- and γ-rays, and Goldblith, Proctor, and Hammerle[82] have also reported the reduction of methylene-blue when dissolved in glycerol, with a similar but less marked effect when methanol was the solvent.

[79] A. J. Swallow, *Biochem. J.*, 1955, **61,** 197.

[80] R. Allinson, B. Coleby, and J. Weiss, *Nature*, 1955, **175,** 720.

[81] C. Piffault, P. Blanquet, and J. Duhamel, *J. Phys. Radium*, 1952, **13,** 138.

[82] S. A. Goldblith, B. E. Proctor, and O. A. Hammerle, *Ind. Eng. Chem.*, 1952, **44,** 310.

The Future of Radiation Chemistry

In the past there has been a tendency to work with rather small doses of radiation. This is partly because the sources so far available have been capable of only a rather limited energy output, and partly because the elucidation of reaction mechanisms is easier when uncomplicated by the presence of appreciable amounts of product. If radiation is to develop in the direction we indicate then there is a need for work with larger doses in order to secure good yields as understood by the organic chemist. Fortunately large sources of radiation are becoming available, and there is considerable scope for discovering new reactions and for developing old ones. Ionising radiations provide a uniquely powerful source of energy, possessing many advantages over traditional sources such as heat and ultraviolet light, and it is likely that the reactions here described represent only a small proportion of those possible, especially in irradiation of mixtures.

Industrial Uses of Ionising Radiations.—Among the most convenient sources for use in laboratories are those made from relatively long-lived radioactive materials, but when more atomic piles are in operation there will be an embarrassingly ready supply of short-lived fission products. Consequently much thought has been given to industrial uses of ionising radiations. With the possible exception of the sterilisation of pharmaceutical products and food, it may be that the largest single use for ionising radiations will be in performing chemical reactions on an industrial scale. This development may take place within 10—15 years.[83] The types of reaction most likely to be commercially feasible are the production of expensive chemicals, needed only in small amounts, and chain reactions where large yields are obtained. Examples of chain reactions are addition polymerisation, chlorination, and possibly depolymerisation at sufficiently high temperatures. The polymerisation of ethylene provides a particularly good example, for by using ionising radiations it may be possible to obviate the high temperatures and pressures otherwise required. Recently there have been several published discussions of the possible industrial utilisation of radiation-chemical processes.[19, 84]

[83] R. Spence, *Chem. and Ind.*, 1954, 1532.
[84] L. E. Brownell, U.S. Atomic Energy Commission Report, 1951, C.O.O.-86 ; G. N. Walton and J. Wright, *Nature*, 1953, **172,** 147 ; Atomic Energy Research Establishment Report, 1953, A.E.R.E.-C/R 1231.