RUSSIAN CHEMICAL REVIEWS
Uspekhi Khimii

July 1966

U.D.C. 541.15:541.124.7:541.141.6

IONIC AND ELECTRONIC PROCESSES OCCURRING IN CONDENSED HYDROCARBONS UNDER THE INFLUENCE OF IRRADIATION

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I. INTRODUCTION

In the present review we shall discuss the "ionic aspects" of radiolysis, that is, we shall attempt to follow the fate of the charged particles which are formed by the action of radiation and to clarify their chemical role in radiolysis. Particular attention will be paid to the condensed phase, because ionic processes in the gas phase have already been widely investigated and their role in chemical reactions induced by radiation is fully recognised. Studies of the ion–molecule reactions, discovered in 1952 by Tal'roze and coworkers, have made an important contribution to the solution of this problem: they deal with the fundamental chemical process following the formation of the ions. Several review articles[1-4] have appeared on this topic, and we shall not discuss it here in detail. Ionic processes in a condensed phase cannot, as a rule, be investigated under model conditions, as for example in the ionisation chamber of a mass spectrometer, commonly used to study ion–molecule processes in the gas phase. We shall often be compelled, therefore, when discussing various processes involving ions, to use analogies with the gas phase and to carry over to the condensed phase the relationships obtained for gaseous systems. This approach is justified when dealing with the radiolysis of organic compounds, whose molecules experience only weak mutual interactions in a condensed phase and behave in a number of respects as if they were in a rigid gas.

The action of penetrating radiation (gamma quanta, X-rays, or electrons) on matter is mainly the result of interactions between the fast primary quanta or electrons and the electrons located in the electronic shells of atoms or molecules. Interactions between primary particles and atomic nuclei can be ignored in radiation-chemical investigations.

With gamma energies of the order of 1 MeV, the fundamental primary process is Compton scattering, which gives rise to fast electrons in the irradiated material. In contrast to external irradiation with electrons, the Compton effect leads to a uniform irradiation of the material, since

it is equivalent to a number of electron sources distributed throughout the bulk.

Irrespective of the nature of the primary radiation, the active particles are essentially fast electrons. At the very beginning of their residence time in the material these electrons have an energy distribution not very different from the initial energy of the penetrating radiation. However, the number of electrons in the material quickly rises as a result of ionisation, and a wider distribution is rapidly set up. At equilibrium, the energy distribution of the electrons covers a spectrum from well below the ionisation energy of the molecules to a value equal to the original energy of the electrons [5].

The cross-sections for the ionisation and excitation processes occurring under the influence of electron impact are a function of the energy of the electrons. A common feature of all these processes in the high-energy region is a decrease in cross-section with increase of energy. However, the radiation yield of ions, or the ratio of the energies expended in ionisation and in excitation, which determines the yield, remains constant [6]. The ratio depends mainly on the distribution of excited states and on the position of the ionisation level in relation to this distribution. Some typical values of mean energies needed to generate electron–ion pairs in gases [7] are listed in Table 1.

Since the lowest electron energies I which will cause ionisation lie in the range 12–15 eV, we conclude from Table 1 that approximately 40–50% of the total irradiation energies listed goes into ionisation processes†. There is no reason to believe that this proportion decreases in a condensed phase. Indeed, electrons in molecules have practically identical energy spectra in the gas phase and in a condensed phase, and the ionisation energy is actually lowered in a condensed phase by the polarisation of the medium caused by the distributed charges [8]. The subsequent fate of the electrons and ions which are formed is the main problem. If they mutually recombine in a time so short that alternative processes involving the ion and the electron cannot compete, there will be no chemical manifestation of the ionisation process. The excited molecule formed by the recombination can be treated as the true forbear of all chemical transformations in the material. This suggestion was first put forward by Samuel and Magee [9], and has since caused the role of ions and their reactions in a condensed phase to be occasionally underrated. If the recombination of the ion and the electron is slower than some other reaction between these charged particles and a third body, ionic reactions can be expected to play an important part in the radiation-chemical processes in condensed media.

TABLE 1.

Molecule	H_2	N_2	O_2	Air	CO_2	CH_4	C_2H_6	C_2H_4	C_2H_2
Mean energy per ion pair, W, eV	36.3	34.9	30.8	33.9	32.8	27.3	24.5	26.1	25.7
Ratio W/I	2.35	2.24	2.55	—	2.38	2.10	2.10	2.48	2.25

† We should note also that the ions can be formed in an excited state, and that this will increase still further the percentage of the energy used by ionisation processes in the primary act.

The generation, motion, and recombination of ions and electrons in a condensed phase is revealed most directly by studies of the electrical conductivity induced in solids or liquids by irradiation. However, conductivity studies alone are insufficient to characterise the chemical role of the ions.

A number of recent papers have dealt with the direct observation of the ionic processes leading to chemical changes in the material, and have stressed the importance of ionic reactions during radiolysis. The most fundamental among these will be discussed below.

We shall deal first of all with studies of the physical properties of the ions formed during radiolysis. The chemical transformations of the ions will be considered next.

II. ELECTRICAL CONDUCTIVITY UNDER THE INFLUENCE OF IONISING RADIATION

1. Free and Bound Charges

The appearance of electrical conductance in a condensed phase under the influence of ionising radiation is evidence that ions and electrons are formed. The pair of charges produced by the ionisation of a molecule can contribute to the current flowing through a specimen in an electric field only if the positive ion and the electron of which it is composed do not recombine with one another. We shall refer to such electrons and ions as "free". The electron ejected by ionisation suffers collisions as it moves away from the ion, and loses its energy. If the kinetic energy of the electron is converted into thermal energy before the electron has moved to such a distance from the ion as to make the coulombic interaction energy between their charges small, the cold electron can turn back and neutralise "its own" ion. There will then be no contribution to the electrical conductivity. Some of the electrons, having a high initial energy, will be able to move to greater distances from their parent ion, and become free. For free electrons the recombination can involve any positive ion with equal probability. Obviously, the yield of "free" electrons will depend on the rate at which energy is lost by the slow electrons in the medium. An approximate calculation of the maximal energy losses consistent with the escape of an electron of initial energy E from the sphere of coulomb attraction can be made as follows.

Let δ be the fraction of its energy which an electron loses at each collision. The number of collisions needed to cool an electron from energy E to kT is then given by

$$j = \frac{1}{\delta} \ln \frac{E}{kT}$$

and the corresponding time is

$$\tau = \frac{j}{N\sigma v} = \frac{1}{\delta N\sigma v} \ln \frac{E}{kT},$$

where N is the concentration of scattering centres, σ the scattering cross-section, and v the mean velocity of the electron. "Freeing" of the electron requires that the diffusion length after time τ should be greater than or equal to the radius of the sphere of action of the coulombic field $r_c = e^2/\epsilon kT$, that is:

$$\frac{\sqrt{j}}{N\sigma} \geqslant r_c \quad \text{or} \quad \delta \leqslant \frac{(\epsilon kT)^2 \ln \frac{E}{kT}}{e^4 (N\sigma)^2}.$$

Taking the mean free path of the electron to be $\lambda = 1/N\sigma = 5$ Å, with $\epsilon = 2$ and $E = 10$ eV, we find $\delta \leq 1.8 \times 10^{-3}$.

Although this estimate takes no account of the drift of the electron in the coulombic field and is therefore only a rough approximation, it does nevertheless show that the δ values required to free the electrons lie very close to the relative energy losses occurring in the elastic scattering of electrons. We can therefore expect a strong correlation between the yield of free electrons and such parameters of the material as the dielectric constant, crystallinity, and vibrational spectrum.

When solids are irradiated at low temperatures the yield of free electrons should increase with dose of radiation, because stabilised charges accumulate in the material as the dose is increased and the spheres of action of their coulombic fields begin to overlap[10]: under these conditions the electrons need only travel a smaller distance from "their own" ion in order to "free themselves".

Studies of electrical conductance are concerned only with "free" electrons and ions, but they reflect also the behaviour of other charges produced during ionisation.

2. Liquids

Measurements of the yield of charges under the influence of ionising radiation have been made mostly in the liquid phase. The currents in liquid ionisation chambers, and their variation with applied electric field, have been measured. It was expected that at high applied fields all the free carriers would reach the electrodes, and the saturation current under these conditions would be a measure of the rate of formation of charges. It was found, however, that although the current through a liquid ionisation chamber increases more and more slowly as the potential is increased, it never reaches saturation. This happens when the current through the chamber varies linearly with the intensity of irradiation, showing that the charges are destroyed only at the electrodes[11]. Hence, one method of determining the yield was to extrapolate this current to an infinitely large field, because the absence of saturation suggested that some other mechanism was operative and competed with the separation of the ions. This method was used to estimate the ion yield of CS_2,[12,13] and also in some liquid saturated hydrocarbons[14] between C_6 and C_{10}. Yields equal to those in the gas phase[13], or close to them[14] (~ 1), were obtained. Obviously, a method involving such a long extrapolation cannot give precise values for the yield, but estimates by this method are capable in principle of giving the total yield of charges formed during irradiation. It is suggested in these papers that the lack of saturation is due to fast recombination of the charges in the tracks, where the ion density is high. An alternative mechanism, which would have a similar effect, is the recombination of the electrons with "their own" ions.

A second group of papers deals with conductance studies at low field intensities[11,15,16]. Under these conditions only a small fraction of the current carriers reach the electrodes, and the free ions and electrons are lost in the bulk. To calculate the radiation yield $G(e)$ one measures the electrical conductivity $\sigma = n\mu e$, where n is the steady-state concentration of current carriers and μ is a mobility defined as the sum of the mobilities of ions and electrons. The steady-state concentration of current carriers n is determined by the rates of recombination and of generation of free charges:

$$n = \left(\frac{GI}{100} \cdot \frac{1}{k}\right)^{1/2}.$$

Here I is the energy of the radiation in eV absorbed by 1 cm³ of the liquid per second and k the recombination coefficient. The latter can be calculated either from the mobility, $k = (4\pi e/\epsilon)\mu$, or determined experimentally from the kinetics of the decay of σ following removal of the irradiation. The mobility of the ions in the liquid under study must be known in order to calculate G. The most direct method of determining the mobility is to measure the time T required for the ions or electrons to travel the known distance l between the points of generation and of detection. The relationship is $\mu = l/TE$, where E is the strength of the field causing the motion of the current carriers. This method has been used to measure the mobility of ions in n-hexane[15,17]. Some values of μ are set out in Table 2.

The temperature variation of the mobility of electrons, measured[17] by emission from a photocathode into n-hexane under the influence of light, has been found to be exponential with an activation energy of 0.14 ± 0.02 eV. This result suggests that an electron in a liquid may spend part of its time in states which are similar to shallow traps in crystals.

The radiation yields of "free" current carriers measured at low field intensities are smaller than in gases; the following values have been reported: 0.2,[11] 0.09,[15] 0.07.[16] These low values are evidence that only a small fraction of the electrons produced manage to escape from "their own" ions. A recent calculation[21] has shown that the low yield can be satisfactorily explained by assuming that ionisation is brought about only by δ-electrons with an energy of 100–200 eV.

TABLE 2.

Current carriers	μ, cm² V⁻¹ s⁻¹ at 300°C				
Positive	—	$5.8 \cdot 10^{-4}$	$4.1 \cdot 10^{-4}$	—	$3.8 \cdot 10^{-4}$
Negative	10^{-3}	$9.2 \cdot 10^{-4}$	$13 \cdot 10^{-4}$	$12.5 \cdot 10^{-4}$	$7.6 \cdot 10^{-4}$
Reference	18	19	20	17	15

3. Solids

The appearance of free charges in a solid organic material under the influence of irradiation is accompanied by an increase in electrical conductivity. Since the majority of radiation-chemical investigations have been carried out on amorphous or microcrystalline organic materials, a rigid application of the band theory is not possible. However, as a matter of convenience in the present discussion, the band diagram can be replaced by an energy diagram showing the distribution of levels corresponding to the ionised states. The minimal energy needed to produce a free electron in an organic material is sometimes called the ionisation potential in the condensed phase. This quantity[8] is lower than the ionisation potential in the gas phase by the polarisation energy $2P$ gained

by bringing the two charges from a vacuum into the condensed phase‡. If the molecules of the material have a positive electron affinity Q, the lowest energy consistent with the formation of a pair of charges not interacting with each other is given by

$$E = I_{gas} - 2P - Q = I_{solid} - Q.$$

The energy diagram of the ionised states in the gas phase and in a condensed phase is shown in Fig. 1. In the "forbidden gap", that is, in the band of levels located between the level of the positive ion of the parent substance and that of the negative ion, we can find ionised states whenever impurity molecules with a lower ionisation potential or a higher electron affinity than the molecules of the major constituent are present in the system. Such levels can be produced also by structural defects. Levels in the "forbidden gap", by which electrons or positive charges can be captured, are usually called traps. In principle, the following can take part in electrical conduction: (1) electrons which are not localised on any molecule, (2) electrons captured by the molecules of the material and undergoing resonance charge transfer of negative ions (for molecules with a positive electron affinity), and (3) positive charges in the molecules of the material undergoing resonance charge transfer of ions. In addition, electrical conduction can, on occasions, result from the transport of

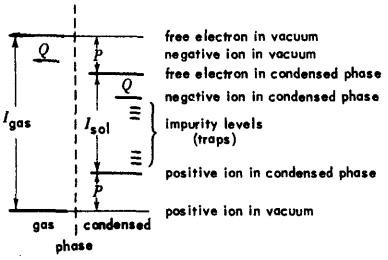


Fig. 1. Energy diagram for ionised states in the gas phase and in a condensed phase.

the ions themselves (either traps which have captured an electron or a hole or charged molecules of the major constituent).

The study of the electrical conductivity of organic substances under the influence of ionising radiation bears some similarity to the study of the photoconductivity of semiconductors and dielectrics. However, in contrast to the effect of light, radiation produces not only current carriers but also new molecules in the host material which can act as traps for the current carriers.

Studies of the electrical conductivity of solid organic materials, and particularly of polymers, have been described in numerous publications [25-33]. The main characteristic of the electrical conductivity observed under irradiation is a dependence of σ upon the dose rate (or intensity) I. In general, it is found that

$$\sigma = n\mu e = \alpha I^{\Delta} \S \qquad (1)$$

where Δ can have any value from 0.5 to 1. The value of Δ is determined by the mechanism of recombination of current carriers. Many solid organic substances give $\Delta \simeq 1$ on irradiation, and $\sigma = 10^{-18} I$ to within two orders of magnitude [34], where σ is expressed in Ω^{-1} cm^{-1} and I (the dose rate) in rad min^{-1}. Ionic conductivity does not appear to play a major role when solid organic substances are irradiated, as evidenced by measurements of the electrical conductivity induced by irradiation in solid heptane [10,35] and polyethylene [33] at liquid nitrogen temperature, when ionic motion is excluded. The electronic conduction processes described by Eqn. (1) are in satisfactory agreement with the theory of photoconduction in the presence of traps [36]. Fowler [37] was the first to apply this theory (to irradiated polyethylene): his scheme describing the participation of traps in the recombination process (scheme *I*) is reproduced in Fig. 2. The figure also shows alternative schemes by which traps can be involved in electrical conduction processes (*II* and *III*). In the first scheme we can assume, to simplify matters, that only the electrons are mobile. In all schemes the electrons, which take part in electrical conduction as long as they remain in the free (non-localised) state, are removed from the sphere of action for appreciable periods when they fall into traps. The time during which they remain untrapped, in the free state, determines their mean effective mobility μ_{eff}, which characterises the electron throughout its lifetime from generation to recombination with a positive ion¶. The extent of filling of the traps is determined by the probability of electrons falling into the traps and by the time of residence of an electron in the trap. As the traps are gradually filled, the electron mobility μ_{eff} increases. If the electron traps are distributed in depth, it is evident that at equilibrium under irradiation the deeper traps will be filled to a greater extent than the shallower traps. The total number of filled traps will depend on the intensity of irradiation, and increase with

‡ In a condensed phase, as in the case of gases, we must distinguish between the "vertical" and the "adiabatic" ionisation potential. The former is determined by an electronic transition in the molecule, and by the electronic polarisation in the medium, without any change in the position of the nuclei of the ionised molecule or of the molecules of the surrounding medium. The adiabatic ionisation potential in a condensed phase is lower than the vertical potential not only because of the different internuclear distance in the resulting ion, but also because of low-frequency polarisation of the medium when polar groups are present. A vertical transition occupies a time of the order of 10^{-15}–10^{-16} s, and is produced by electron impact ionisation or ionisation by light quanta. The low-frequency polarisation is set up, according to the properties of the medium and the temperature, in a time of 10^{-11}–10^{-13} s after the appearance of charges in the medium, and has the effect of placing the electrons and the positive charges in polarisation wells of a peculiar kind. The term polarons has been proposed in the theory of dielectrics for electrons of this type [22]. In polar media such as water and alcohols, polarons (solvated electrons) have been detected experimentally [23,24].

§ In general, electrical conduction involves both electrons and "holes". The latter term refers to positive charges which are mobile by virtue of resonance charge transfer processes. Hence, $\sigma = \mu_h n_h e + \mu_e n_e e$. In order to simplify the problem, it is often assumed that the contribution of carriers of one type can be ignored in comparison to that of carriers of the opposite sign, so that $\sigma = \mu n e$, where n is the concentration of carriers whose contribution to electrical conduction is the more significant and μ their mobility.

¶ When using the mobility μ_{eff}, the expression for the electrical conductivity becomes $\sigma = \mu_{eff} n_n e$, where n_n is the concentration of all negative charges in the material.

increasing intensity. This, in turn, will raise the electron mobility μ_{eff}. Thus, an increase in radiation intensity will, on the one hand, decrease the lifetime of the current carriers by increasing the probability of electron–ion recombination, and on the other hand it will increase the effective mobility of the current carriers. These factors are very sensitive to the distribution of the traps in depth. Thus, in scheme *I* of Fig. 2 we can assume an exponential distribution in depth[37]: this gives the number of traps lying in the range from E to $E + \Delta E$ below the free-electron level as

$$M_E dE \sim e^{-E/kT_i}\ dE,$$

where T_i is a constant characteristic of a particular substance. It turns out that $\Delta = T_i/(T + T_i)$. By suitable choice of T_i we can have any value of Δ from 0.5 to 1, but this value remains constant over a wide range of radiation intensities. The lack of dependence of Δ upon I is the strongest argument in favour of the choice of an exponential energy distribution for the traps.

A relation of the type $\sigma = \alpha I^{\Delta}$ can be obtained if all the traps in the system lie at the same depth. However, the value of Δ will then vary with intensity of irradiation. Thus, at very low intensities, when the lifetime of a current carrier is much greater than its trapped time, $\Delta = \frac{1}{2}$. At high intensities Δ tends towards unity, but it drops back to $\frac{1}{2}$ when most of the traps are filled. The large range of intensity values which has to be covered in order to observe the slow variation of Δ with I does not allow us to identify the type of distribution of the traps with confidence from the measured values of Δ alone: experimental measurements of this quantity usually fall somewhere between 0.5 and 1 and appear to be constant at this intermediate level[38]. For polyethylene it is reported[37] that $\Delta = 0.7$.

If the positive charges formed by irradiation are mobile, electrons captured in traps can recombine with the positive charges directly, without being emitted into the conduction band. This scheme is shown in Fig. 2, *II*. Lastly, we can have a third type of electrical conduction process, shown in Fig. 2, *III*, in which a current carrier is emitted from a deep trap to the conduction band as a result of energy transfer from the radiation field.

We cannot make an unambiguous choice between the various schemes of carrier recombination and trap filling on the basis of measurements of the quantity Δ. Measurements of the kinetics of the growth or decay of electrical conductivity following exposure to or removal from irradiation are also of little help, because any of the models can be made to agree with experiment by suitable choice of distribution of the traps.

The most important conclusion to be drawn from studies of electrical conductivity is that the role of traps in the recombination of free electrons is established. By assuming an exponential energy distribution of traps it has been possible to estimate the concentration of traps present in polyethylene[37] and in octacosane[39] before irradiation. Since this concentration was found to be independent of the degree of purification of the material, it was concluded that traps in saturated hydrocarbons are not impurities but structural defects (possibly perturbations in the short-range order in the molecular distribution[39,40]). The concentrations of traps were found to be very large ($\sim 10^{20}$ cm^{-3}).

4. Accumulation of Stabilised Charges Under Low-Temperature Radiolysis

The discovery of thermally stimulated currents in saturated hydrocarbons irradiated at low temperatures[41–43] is a direct proof of the accumulation of current carriers in traps. The thermally stimulated current peak shown in Fig. 3 appears when irradiated specimens are allowed to warm up and is associated with the emission of current carriers from the traps and their recombination. The appearance of conductance on heating irradiated specimens suggests that both negative and positive charges are stabilised at low temperatures.

The role of traps in recombination processes has been investigated by attempting to introduce new traps into the specimen and monitoring changes in electrical conductivity under irradiation. Thus, Wintle[44] examined the changes in the nature of the σ–I relationship for polyethylene brought about by previous exposure of the specimen to a large dose of radiation. The relationship was found to become linear, with $\Delta = 1$, in keeping with the formation of deep traps as a result of irradiation. The nature of these traps was not characterised. Yakovlev and Frankevich[10] studied the electrical conductivity of n-heptane at liquid nitrogen temperature as a function of irradiation with a constant flux of fast electrons, and found that σ under irradiation falls as the total dose of radiation is increased. They were able to relate this drop in σ to the known concentration of free radicals which had accumulated in the specimen under the

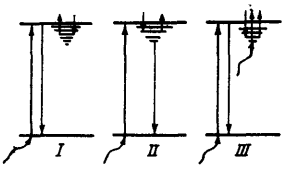


Fig. 2. Distribution of trapping levels and recombination mechanism:
I) recombination of a free electron with an ion; thermal emission of electrons from the traps; II) recombination of an electron captured in a trap with a mobile positive charge; III) recombination of free electrons with ions; excitation of trapped electrons by the transfer of radiation energy.

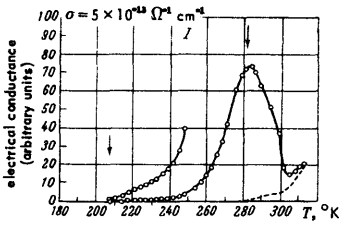


Fig. 3. Thermally stimulated conductance curve in an irradiated paraffin[41,42], dose 50 Mrad. The broken line shows the electrical conductance of the paraffin in the absence of irradiation. The initial section of the curve is replotted on an enlarged scale.

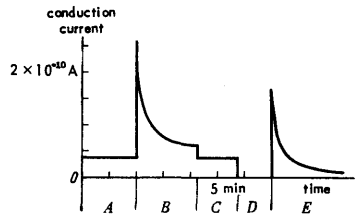


Fig. 4. Variation of the conduction current through a specimen of n-heptane under irradiation (sections *A* and *C*), combined irradiation and illumination (section *B*), and illumination of an irradiated sample (section *E*). Dose rate 0.12 Mrad min^{-1}.[47]

influence of radiation and behaved as traps for current carriers, and to calculate the concentration of traps present in the specimen before irradiation. The concentration was found[45] to be $10^{19}-10^{20}$ cm^{-3}. The suggestion that free radicals in saturated hydrocarbons can act as traps for charges at low temperatures was first put forward by Tal'roze[46].

The reported photoconductivity[10,35,47] of saturated hydrocarbons during and after irradiation is further confirmation of the capture and accumulation of electrons in hydrocarbons during irradiation. Photoconductivity has been observed also in irradiated aromatic hydrocarbons[48]. Fig. 4 shows typical plots of the current through a specimen of frozen n-heptane, recorded during irradiation with fast electrons and/or visible light[47]. The conductivity peak observed upon exposure to light is due to the emission of current carriers from traps, and the decay is due to the destruction of traps. The amplitude of the photoconductivity peak is proportional to the concentration of trapped current carriers, and can be used as a measure of this concentration. By measuring the amplitude of the photoconductivity as a function of dose Yakovlev and Frankevich[10] were able to monitor the filling of the traps during irradiation and to estimate the limiting concentration of filled traps. This was found to be $10^{17}-10^{18}$ cm^{-3}, that is, a small fraction of the total concentration of traps.

The low degree of filling implies a mechanism of annihilation of the traps other than thermal excitation, whose probability at a temperature of -196°C is extremely small. Such a mechanism is operative in schemes *II* and *III* of Fig. 2: it involves recombination with mobile "holes"[51] and excitation of trapped current carriers by the resulting energy transfer. It is probable that the positive charges (or "holes") are able to contribute to conduction for a short period following their generation, whilst they remain excited, and become stabilised only after their excitation energy has been dissipated.

The following observations are relevant to a discussion of the factors which cause freezing of the holes. Obviously, the motion of positive charges implies resonance charge transfer between neighbouring molecules. The positive charges in saturated hydrocarbons are localised at individual $-CH_2-$ groups. The ionisation potential of a $-CH_2-$ group depends on the position of the group within the molecule, being lower for central groups and increasing towards the ends of the molecule. This is because the positive charge polarises the molecule, and the gain in polarisation energy is greatest when the charge is located centrally. The existence of a difference in ionisation potential, which can be as large as 0.3 eV for 2-3 $-CH_2-$ units, makes the movement of holes very slow at low temperature. Charge transfer occurs by an electronic mechanism, and does not involve, in keeping with the Franck-Condon principle, any change in the relative positions of atoms. However, the mean interatomic distances in an ion and in a neutral molecule are different, and vibrational excitation of the ions and molecules is needed for charge transfer: this can significantly retard the charge transfer at low temperatures.

Furthermore, positive charges can fall into traps which they "dig" for themselves by undergoing ion-molecule reactions. Thus, the positive charge formed by the exothermic reaction

$$\begin{array}{l} -CH_2-CH_2^+-CH_2- \\ -CH_2-CH_2-CH_2- \end{array} \longrightarrow \begin{array}{l} -CH_2-CH_3^+-CH_2- \\ -CH_2-\dot{C}H-CH_2- \end{array}$$

on a $-CH_3^+-$ group cannot even move to one of the neighbouring $-CH_2-$ groups, because this would involve overcoming a potential energy barrier†.

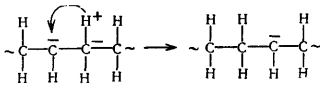
One possible cause of the low degree of filling of the traps by electrons could be the excitation of the electrons by the energy of the radiation, a term which includes here all forms of energy present in the irradiated material: non-equilibrium vibrational excitation energy, electronic excitation energy, light, and slow electrons (sometimes called "subelectrons"[49,50]). The fractional filling of the traps by electrons, n_-/N_t, is a very sensitive function of the probability of excitation of a trapped electron. For scheme *III* of Fig. 2 it can be shown that

$$\frac{n_-}{N_t} = \sqrt{\alpha}\sqrt{\frac{\sigma_c}{\sigma_r}}\cdot\sqrt{\gamma},$$

where α is the relative probability of excitation of a valence electron and of an electron captured in a trap, γ the number of traps expressed as a fraction of the total number of molecules, σ_r the cross-section for the recombination of an electron with a positive ion, and σ_c the cross-section for the capture of an electron by a neutral trap.

Calculation shows that even for $\alpha = 10^{-2}$ the fraction of filled traps is $n_-/N_t = 10^{-2}$, in qualitative agreement with the experimental value.

The concentration of all charges which accumulate in various saturated hydrocarbons has been measured[52] by studying the relaxation polarisation which appears after irradiation of the materials at low temperature (-196°C) with a 10-50 Mrad dose: the value obtained was 10^{19} cm^{-3}. Since the relaxation time of the charges was found to increase monotonically with molecular chain length in the hydrocarbon series (C_6-C_{12}, C_{25}, polyethylene) examined, a model was put forward according to which a charge localised on a deep trap (a free radical) can move as a result of proton transfer:



This process has a relatively low activation energy for intramolecular transitions (estimated[52] to be 0.06 eV), and accounts for the comparatively high mobility of positive charges within the limited potential wells associated with

† It should be noted that movement of the charge within the molecule may still be possible owing to resonance proton transfer.

the molecules. Limited motion of this type manifests itself as relaxation polarisation, observed when irradiated hydrocarbons are allowed to warm up. Molecular transitions giving rise to electrical conduction in the sample after irradiation and heating appear to need a higher activation energy (0.6 eV, as estimated from the initial portion of the thermally stimulated current curves).

5. Determination of the Electron Yield in the Solid Phase

Gemant[53] made a direct estimate of the yield of electrons in solid hydrocarbons, by measuring the time constant T for the establishment of electrical conduction in a paraffin film enclosed between two electrodes and irradiated with β particles. The intensity of irradiation was low, and the lifetime of the charges was determined only by the transit time of the current carriers between the electrodes. Under these conditions the radiation yield of charges taking part in electrical conduction is 0.036 for 100 eV, and their mobility is 5×10^{-8} cm^2 V^{-1} s^{-1}. This value is fairly close to the yield of free charges measured in liquid n-hexane[11]. The low mobility is evidence that either the current carriers move "from trap to trap" or the mobile species are ions.

Frankevich and Balabanov[54] attempted to measure the yield of all charges formed during bombardment of a paraffin with electrons. A thin film of paraffin, enclosed between two electrodes, was irradiated by a short pulse of electrons of energy 3–5 keV, and the current pulse in the specimen circuit due to the motion of the resulting charges in an electric field was measured. Immediately after their generation all charges act as current carriers and contribute to the conduction current. If a high concentration of traps is present in the specimen some of these charges are captured by traps, and charge recombination (which "confiscates" the contribution of the charges to the conductivity) takes place with a time constant equal to the lifetime in the traps. Measurements showed[54] that a large proportion of the electrons actually return to "their own" ions, and that their trapped time for the C_{25} paraffin at room temperature amounts to tens of seconds. Measurements of the conductivity pulse give $G\mu\tau = 2.6 \times 10^{-12}$ cm^2 V^{-1}. Hence, and from the maximum diffusion length of an electron in the electric field — which for an electron which does not become free cannot exceed $r = \sqrt{e/\epsilon E}$, where E is the external field strength and ϵ the dielectric constant — the yield of electrons captured by traps upon irradiation could be calculated, and the value obtained was $G > 1$. These results also showed that each electron, on the average, migrates more than 30 Å from "its own" ion if the total radiation yield of electrons is taken to be $G = 3$.

III. METHODS OF DETERMINING IONS IN CONDENSED HYDROCARBONS WHICH DO NOT DEPEND ON THE ELECTRICAL PROPERTIES OF THE IONS

In addition to their electric charge, which is their most fundamental property, ions have a number of other properties, less specific but nonetheless characteristic, which can be used to identify the ionised states formed in an organic compound by the action of radiation. The following properties have been used to detect ions: the magnetic moment (for paramagnetic ions), the absorption spectrum, and the light emitted by the recombination of ions with electrons.

Many workers have observed a light-sensitive line, which disappears on exposure to visible light, in the ESR spectrum of alcohols[55,56], polyethylene, paraffin, and rubbers[57] irradiated at low temperatures. Sensitivity to light in the visible region suggests weak bonding of the electron, and justifies the conclusion that this ESR line is due to electrons held in traps of some kind. The presence of trapped electrons is confirmed by the development of colour on irradiation and by the thermoluminescence of hydrocarbons irradiated at low temperature and allowed to warm up[55,58-60]. Heating the specimens causes luminescence and at the same time bleaches them. It has been shown[61,62] that the luminescence appears at temperatures corresponding to phase transitions in the irradiated material, and is associated with faster diffusion of the charged particles. The luminescence centres are usually provided by some impurity present in the material which is excited by acquiring the energy evolved by the recombination of charges. The recombination does not involve emission of the electrons from the traps: this follows from the observation that the depth of the traps as deduced from the photoluminescence excitation spectrum in irradiated hydrocarbons (n-hexane, nonane, 2,4-dimethylundecane, tetradecane, cyclohexane, dicyclohexyl-4-decane, polyethylene)[63] is fairly large (2–3 eV) and does not agree with the depth measured by the appearance temperature of the thermoluminescence peak. The photoluminescence excitation spectra of irradiated hydrocarbons have been found[63] to depend on the total dose of radiation. At high doses (> 10 Mrad) the spectrum is displaced towards the short-wave region, pointing to the appearance of new, deep traps on irradiation. These traps are, very probably, free radicals[45].

Many workers have studied the appearance of ions in two-component systems (solid solutions), because these systems offer the possibility of identifying certain ions either by their absorption spectra or by their ESR spectra. Therefore, additives able to give rise to such ions offer a means of monitoring their formation and accumulation under irradiation.

It should be noted that the formation of ions of the second component in two-component systems can occur by direct ionisation, but also as a result of charge transfer, excitation transfer, or ionisation by subelectrons, that is, electrons whose energy is less than the ionisation potential of the molecules of the major component. At low additive concentrations we can ignore direct ionisation, but it is not always possible to choose unequivocally among the other possible processes.

Bagdasar'yan and his coworkers[64-66] have studied the formation of positive ions of aromatic amines in matrices of methylcyclohexane, isopentane, and poly(methyl methacrylate). Samples were exposed to γ-radiation at -196°C. The ions of aromatic amines were identified by their known absorption spectra. The yield of positive ions of the amines in a hydrocarbon glass was 0.16 (at an impurity concentration of 0.005 M) on the basis of the energy absorbed by the whole of the sample; in poly(methyl methacrylate) G(ions) = 3 at an impurity concentration of 0.1 M. The limiting concentration of ions was 10^{-5} and 10^{-3} M in the two experiments respectively, and did not increase when the additive concentration was increased. The authors suggest that the amine ions are formed by the capture of positive charges (initially generated in the matrix) by solute molecules. However, they do not exclude the possibility of ionisation of the amines by excitation energy gained from the matrix[67].

The formation of positive ions of *NN*-dimethyl-*p*-phenylenediamine (DMPD) was studied spectroscopically by introducing the amine into various matrices[68] and than irradiating with γ-rays at -196°C. A high yield ($G \simeq 2$) of DMPD ions was obtained in non-polar media, but in polar media (alcohols) the yield was much lower under otherwise identical conditions. Addition of an electron-acceptor impurity to the matrix as well as the amine raised the yield of DMPD cations to 4 in non-polar media and by a small amount in polar media. These results were interpreted in terms of the capture by amine molecules of positive charges formed by ionisation of the matrix. The small yield of cations in polar media is tentatively ascribed to an ion–molecule reaction observed in the gas phase[69], of the type

$$C_2H_5OH^+ + C_2H_5OH \longrightarrow C_2H_5OH_2^+ + C_2H_5O,$$

leading to positive charge "capture". The presence of acceptor molecules lowers the mobility of electrons and precludes to some extent their recombination with positive charges.

The formation of negative ions has been observed spectroscopically and by ESR in poly(vinyl chloride) and poly(methylmethacrylate) containing electron-acceptor impurities (quinones, polycyclic aromatic compounds, etc.)[70]. These were irradiated with γ-quanta at -196°C. The concentration of additives was between 0.03 and 0.6 mole %. Under these conditions the yield of anions, calculated on the basis of the energy absorbed by the acceptor molecules in the system, amounted to 100–1000. This is evidence for energy transfer from the matrix to the impurity. The authors suggest that the impurity directly captures an electron which would otherwise by captured by a polymer molecule. They point out that the retrapping of an electron by an impurity completely suppresses the formation of conjugated bonds and the appearance of colour in poly(vinyl chloride) upon irradiation.

Guarino and coworkers[71,72] have reported a systematic investigation of the formation of negative ions in hydrocarbon matrices. Naphthalene or biphenyl impurities were introduced into a matrix of tetrahydro-2-methylfuran (THMF). The absorption spectra and the extinction coefficients of the negative ions produced from these molecules are known, since the ions can be prepared chemically by reduction with alkali metals (with formation, for naphthalene, of $Na^+C_{10}H_8^-$). The samples were irradiated with γ-rays at -196°C. In a glassy matrix of THMF containing naphthalene the limiting yield of $C_{10}H_8^-$ anions was found to be 2.6; with biphenyl as the impurity the yield (of $C_{12}H_{10}^-$ ions) was 3.2. In hydrocarbon glasses containing the same impurities the anion yield was 1.1 and 1.7 respectively, whilst in an ethanol matrix the yield of anions was 2.94. When the impurity concentration was of the order of 0.05 mole %, the yield was close to unity in all media. Evidently, as in any other two-component medium, the retrapping of an electron ejected from a molecule of the solvent is not the only possible mechanism of formation of ions of the minority component. Ionisation by excitation transfer or by subelectrons is also possible. Further experiments were needed to substantiate the authors' contention that the measured electron yields applied to free and thermally generated electrons formed by the ionisation of the substrate. Thus, it was found that an absorption band which can be bleached by light is formed in THMF even in the absence of added impurities. When the absorption band of the matrix was bleached using a specimen which had been irradiated in the presence of impurities it was found that the concentration of impurity ions rose. This points to the transfer of electrons, initially stabilised in the matrix, to the impurity molecules. The observed competition between two different impurities added to THMF[72–74] is further evidence that the impurity molecules act only as acceptors of electrons generated in the matrix. Thus, if THMF contains only naphthalene (at a concentration of 0.11 mole %) the yield of $C_{10}H_8^-$ ions is 1.63, but the value is lowered when competing substances are added. The decrease caused by various "secondary" impurities is a relative measure of their electron-capturing efficiency. The formation of anions by electron retrapping must involve the scheme

$$M \rightarrow M^+ + e$$
$$X + e \rightarrow X^-$$
$$Y + e \rightarrow Y^-,$$

where M is a molecule of the major constituent, and X and Y are impurity molecules.

If X^- is identified with the $C_{10}H_8^-$ anions, whose concentration can be measured, the measured yield G_{X^-} is related to the impurity concentrations C_X and C_Y as follows:

$$\frac{1}{G_{X^-}} = \frac{1}{G_e^0} + \frac{\sigma_Y}{\sigma_X}\frac{C_Y}{C_X}\cdot\frac{1}{G_e^0}.$$

This formula is correct if the $C_{10}H_8$ molecules capture all the electrons in the absence of a "second" impurity: G_{X^-} is equal to G_e^0 when $C_Y = 0$. Table 3 lists some relative capture efficiencies (σ_Y/σ_X) for electrons, measured experimentally[72] with different Y molecules as the "second" impurity.

The series of relative electron-trapping efficiencies obtained is consistent with the known trapping properties of many of these molecules towards thermal electrons. It was found that the lower the threshold energy in the plot of electron capture cross-section against energy, the more effectively molecules behave in competing for electron capture during radiolysis. The threshold energies for electron capture by HI and HCl molecules are 0 and 0.66 eV respectively; the threshold energies for CCl_4 and $CHCl_3$ are 0.03 and 10 eV. In keeping with these figures, we see from Table 3 that HI molecules are mo efficient electron acceptors than HCl; CCl_4 molecules are much more effective than CH_3Cl. Moreover, it was found that the relative electron trapping efficiency of these molecules increases in the same order as their polarographic half-wave potential.

TABLE 3.

Y	CH_3Cl	C_2H_5OH	C_6H_6	BF_3	CH_3COCH_3	H_2O	$CH_3(CH)_2CH_2$	NO	N_2O
σ_Y/σ_X	0	0	0	1	1	1	2	3	4

Y	C_6H_5Br	$CH_3CHClCH_3$	HCl	C_2H_5I	O_2	$C_6H_5CH_2COCl$	HI	CH_3I
σ_Y/σ_X	5	5	5	6	9	10	11	12

Y	$CHCl_3$	$CH_3CO_2CH_2C_6H_5$	CCl_4	$CHBr_3$	C_6H_5CHO	SO_2	CBr_4	I_2
σ_Y/σ_X	15	17	20	20	22	23	25	37*

* $\sigma_{I_2} = 3.2 \times 10^{-15}$ cm^2.

Similar results were obtained[74] by adding biphenyl and various benzene derivatives to a THMF matrix. The measured relative electron trapping efficiencies (σ_Y/σ_X) are set out in Table 4 (where X = biphenyl).

The results of these investigations[71-74] provide convincing proof that the yield of electrons which can be trapped by various impurities is high in hydrocarbons, and corresponds approximately to the yield of electrons in the gas phase.

By using flash irradiation, which can generate a high concentration of ions, it has been possible to estimate the ions in the liquid phase. Thus, an absorption spectrum has been observed[75] in the region of 2970 Å after flash radiolysis of liquid 2-methylpropene. Trimethylcarbonium ions are known to absorb in this region. The lifetime of the ions was 0.05 s at -15°C. These experiments are similar to those which revealed the presence of solvated electrons in water during irradiation[24].

The overall conclusion from all the data presented in Sections II and III is that the work published so far provides sufficient grounds for the confident assertion that electrons and ions are formed and have an appreciable existence in a condensed phase.

The lifetime of electrons and ions before they mutually recombine is such, even for recombination in pairs, that processes involving the capture of electrons by traps, by specially added acceptor molecules, and therefore also by electron-acceptor radiolysis products, can compete with the electron–ion recombination process. We may conclude from the results discussed above that the following are the most important processes involving charged particles in an organic material:

ionisation	$M + e \rightarrow M^+ + 2e$
recombination of an electron with "its own" ion	$M^+ + e \rightarrow M^*$
electron capture by impurities competing with recombination	$T + e \rightarrow T^-$
recombination of T^- ions (or e^-) with M^+	$T^- + M^+ \rightarrow$ products

If the time during which M^+ ions, and also X^- and T^- ions, can exist is long enough for these ions to take part in ion–molecule reactions, the products of these reactions will take part in the recombination process.

In the liquid phase the time of separate existence of electrons and ions is determined by the time which they take to diffuse towards each other from distances not exceeding r_c but greater than 30 Å (see p. 493). If we assume a mobility for electrons in n-hexane[17] of 10^{-3} cm^2 V^{-1} s^{-1}, a typical lifetime of charges in an organic liquid works out to[76]:

$$\tau = \frac{\varepsilon}{3\mu e^2} r_c^3 \simeq 10^{-7}\ \text{s}.$$

For free electrons the lifetime is very much greater, and depends on the total concentration of ions. However, the yield of free electrons is no more than 3–5% of the total, as was pointed out above.

The existence of two groups of electrons upon irradiation, with widely different lifetimes for recombination, was stressed by Williams[76] in his study of liquid cyclohexane. He showed that addition of a low concentration of ND_3 to cyclohexane leads to the formation of HD molecules, the yield being independent of the impurity concentration over the range 10^{-4}–10^{-2} M and increasing with $\sqrt{[ND_3]}$ at higher concentrations. Since the formation of HD was shown to occur by the process

$$ND_3 + C_6H_{12}^+ \longrightarrow ND_3H^+ + C_6H_{11},$$
$$ND_3H^+ + e \longrightarrow NH_3 + D \text{ (and also } NH_2D + H)$$
$$D + C_6H_{12} \longrightarrow HD + C_6H_{11},$$

it follows that the measured yield of HD is a measure of the number of charges which can be captured by ND_3 (to give ND_3H^+). The lack of dependence of the yield of HD upon the concentration of additive is evidence that the lifetime of at least some of the charges is very long: this fraction of the charges is estimated to be formed with a yield of 0.08, in good agreement with the yield of free carriers[11,15]. The lifetime of the charges formed in very much greater yield was estimated to be 10^{-7} s.

In a solid phase, and particularly at low temperatures, the lifetime can be quite high, and it is always higher than in the liquid phase.

TABLE 4.

Impurity	Biphenyl	Triphenylene	Phenanthrene	o-Terphenyl	Cycloheptatriene	Pyrene
σ_Y/σ_X	1	1.04	1.22	1.40	1.94	1.95

Impurity	1,2-Benzanthracene	Triphenylethylene	Tetraphenylethylene	Anthracene	Hexamethylbenzene
σ_Y/σ_X	2.70	2.60	2.76	2.76	2.80

IV. REACTIONS OF CHARGED PARTICLES IN A CONDENSED PHASE

1. Main Types of Reaction

The ions and electrons formed in a condensed phase are active particles, free to take part in many chemical reactions. The high activity of charged particles has been demonstrated in many investigations of ion–molecule processes in the gas phase, showing that exothermic or athermic ion–molecule reactions involve a negligibly small activation energy. Since the lifetime of ions in a condensed phase is greatly in excess of the time between collisions (10^{-13} s), it is obviously possible for the ions to take part in various reactions. In consequence, ionised products of these reactions can often take part in the recombination process instead of the molecules initially ionised.

Processes involving charged particles during their lifetime can have a profound effect on the chemical action of radiation. Among these processes, the following are the most important.

Processes with the participation of positive charges: unimolecular decomposition; positive charge transfer to molecules of lower ionisation potential than the molecules of the substrate; ion–molecule reactions.

Processes with the participation of electrons: electron transfer to molecules of higher electron affinity than the molecules of the substrate or to traps of structural origin;

unimolecular decomposition of a molecule containing a trapped electron; ion–molecule reactions.

The chain of transformations involving positive and negative charges ends when the charges recombine.

In most instances, workers can critically assess various processes in a condensed phase by referring to the considerable fund of experimental data on the formation of stable radiolysis products. In a condensed phase it is not possible as a rule to examine in detail any particular elementary reaction, including reactions between ions and molecules, by observing the initial particles and their transformation products, as can be done in the gas phase. Therefore, experimental results can often be "satisfactorily" explained by different mechanisms. In these circumstances, the most valuable investigations are those offering some direct evidence that the primary particles leading to the observed product by a clearly defined reaction were ions.

The main criterion of whether any given reaction proceeds with the participation of charged particles is the energy of the reaction. One usually refers to the published heats of the corresponding reactions in the gas phase. This can be justified for processes not accompanied by the disappearance of charges, because a condensed phase lowers the ionisation potential of molecules by the polarising effect of the medium and ion solvation but has no effect on the "neutral" properties of molecules. The lowering of the ionisation potential on changing from the gas phase to a condensed phase drastically decreases the exothermicity of ion recombination processes. Processes involving ions and electrons will be examined in detail in the following subsections.

2. Dissociation of Ions

A positive ion, usually in an excited state when first formed, very quickly (in 10^{-8}–10^{-13} s) loses its excitation energy by collisions with the surrounding molecules.

Dissociation of an excited ion can occur only if the resulting fragment is able to escape from its partner by diffusion: otherwise, the cage effect[77] causes recombination of the ion. It follows that, in practice, the only possible products of dissociative ionisation in a condensed phase are an H atom or a proton. An ion can dissociate from its ground state without any restriction as to the residues only if energy is evolved[78]. A thermochemical calculation shows[79] that dissociation is energetically favourable when, for example, an alkene ion is formed from a saturated hydrocarbon:

$$C_6H_{14}^+ \longrightarrow \begin{cases} \longrightarrow \textit{trans}\text{-}2\text{-}C_6H_{12}^+ + H_2\ (+\ 4\ \text{kcal mole}^{-1}) \\ \longrightarrow \textit{trans}\text{-}3\text{-}C_6H_{12}^+ + H_2\ (+\ 5\ \text{kcal mole}^{-1}). \end{cases}$$

The attachment of an electron to a molecule can also lead to dissociation in apparent contradiction to the cage effect: dissociation of this type occurs if the electron affinity of the resulting fragment is greater than the bond dissociation energy. Dissociation processes of the type $RX + e \rightarrow R + X^-$, well known in mass-spectrometric investigations, are found to be exothermic and to have a threshold at thermal electron energies. A similar process has been observed[80] in solid hydrocarbons containing small amounts of $C_6H_5CH_2Cl$. When an electron, freed from a trap by the action of light in irradiated methyltetrahydrofuran, becomes attached to a $C_6H_5CH_2Cl$ molecule, the formation of $C_6H_5\dot{C}H_2$ radicals can be observed in the solid phase. Similar results have been obtained in studies of other additives of the type RX (where $R = C_6H_5\dot{C}H_2$; $X = CH_3COO$, CH_3O). The efficiency of various additives towards electron capture depends critically on the appearance potential of the X^- ions in the dissociation process, and varies in the same sense as this potential.

3. Charge Transfer

The interaction between positive charges and their surrounding molecules can lead to two types of effect. The first, charge transfer, cannot lead to chemical changes in a homogeneous medium; its only effect is to facilitate the diffusional transfer of charges. In two-component or multicomponent media charge transfer enables the positive charge to become localised on the molecules of lowest ionisation potential. The energy of the ionisation process, given out when a positive and a negative charge recombine, is evolved mainly at these particular molecules[81,82]. This may be the cause of deviations from the so-called law of radiation-chemical additivity (sometimes also termed the "law of mixtures"). The deviation consists in the following: the fraction of the total yield of products contributed by the decomposition of these "acceptors" of energy is higher than expected by considering only what fraction of the energy has been directly imparted by the radiation to the molecules of low ionisation potential. If the charge transfer process is sufficiently effective, the molecules of low ionisation potential will behave as protective additives which concentrate on themselves the main effect of the radiation and thus protect the surrounding medium. According to their chemical stability, these impurities can decompose or they can scatter the energy, the protection being of the "sacrificial" or the "sponge" type in the two cases respectively[83]. It should be noted that charge transfer effects can play an essential role also in the radiolysis of one-component systems, because new molecules are formed in the course of radiolysis and these can concentrate on themselves an increasing fraction of the radiation energy if their ionisation potential is lower than that of the molecules of the major constituent of the medium.

The deviations from the law of mixtures reported so far are very numerous[84,85]. They can be explained, in principle, by the most diverse mechanisms of energy transfer, charge transfer being but one of many possibilities. Hardwick[86] has pointed out that the departures from the law of mixtures in two-component solutions of aliphatic hydrocarbons are always in the sense of energy transfer to the molecules of lower ionisation potential. This conclusion was reached from a study of the yield of hydrogen, which was a product of the decomposition of each of the components of the mixture (n-hexane–neohexane, n-hexane–2,3-methylbutane, and many others). The law of mixtures predicted a hydrogen yield varying linearly with the composition of the mixture, but in practice, owing to energy transfer, this relationship was not observed.

Molecules which behave as charge acceptors, that is, those of lower ionisation potential, can also act as acceptors of excitation energy, because their electronic excitation levels are usually lower. This phenomenon often militates against a definite clarification of the mechanism of energy transfer.

Many workers have examined, spectroscopically or by ESR methods, the state of impurities added to an irradiated substance which have a protective action on the specimen. It was found that the molecules of the additive become ionised. Thus, when poly(methyl methacrylate) is protected from degradation by adding aromatic amines, positive amine ions are detected spectroscopically[64]. The radiation yield of these ions is equal to the fall in the yield of the chain-breaking process in the polymer. Addition of electron-acceptor impurities (quinones, polycyclic aromatic compounds) to poly(vinyl chloride) (PVC) suppresses[79] the formation of conjugated bonds in the PVC and greatly lowers the yield of HCl. This, evidently, results from the transfer of a charge (an electron) to the acceptor. The spectrum of the negative ions of the impurity has been examined by ESR. Studies illustrating the transfer of positive[65-68] and negative[56,71-74] charges to molecules of impurities specially added to hydrocarbon substrates at low temperatures have already been considered in the previous subsections.

4. Ion–Molecule Processes

Ion–molecule reactions are the second type of process in which ions can take part. Two basic types of reaction have been identified in hydrocarbons in the gas phase: reactions involving the transfer of heavy particles such as an H atom, a proton, or a hydride ion, and reactions leading to the synthesis of a C–C bond[2,4,46]:

$$R'H + R''H^{+} \longrightarrow R'H_2^{+} + R'' \quad \text{(proton transfer)},$$

$$R'H + R''H^{+} \longrightarrow R' + R''H_2^{+} \quad \text{(H atom transfer)},$$

$$R'^{+} + R''H \longrightarrow R'H + R''^{+} \quad (H^{-} \text{ ion transfer}),$$

$$R'H^{+} + R''H \longrightarrow R'R''^{+} + H_2 \quad \text{(synthesis of a C–C bond)}.$$

In a condensed phase these reactions can act as a source of free radicals and determine the formation of cross-links. The small temperature dependence of the radiation yield of cross-linking in saturated hydrocarbons and the possibility of inhibiting cross-linking by adding suitable impurities[87,88] have been interpreted as an indication that ion–molecule reactions are responsible for the formation of cross-linked structures. Various reactions have been suggested:

$$(1)\ RH + RH^{+} \longrightarrow RR + H_2^{+} \ [89]$$

$$(2)\ RH + RH^{+} \longrightarrow RR^{+} + H_2 \ [90]$$

$$(3)\ RH^{+} + R \longrightarrow RR + H^{+} \ [91]$$

$$(4)\ RH + RH^{+} \longrightarrow RH_2^{+} + \dot{R}; \quad RH_2^{+} + e^{-} \longrightarrow H_2 + \dot{R}; \quad \dot{R} + \dot{R} \longrightarrow RR \ [92]$$

Thermochemical calculations give the heats of these reactions as -4.72, 0, -2.50, and 9 eV respectively, so that at least two of them, (2) and (4), could control the formation of cross-linking. Available data do not allow an easy choice between these two alternatives, because their occurrence in a condensed phase has not been directly reported. The distribution of isomers of the C_{12} dimer formed during the low-temperature radiolysis of n-hexane, investigated by Kevan and Libby[92], can be satisfactorily explained on the basis of reactions (2) and (4).

The positive charge, having taken part in an exothermic ion–molecule reaction, is found in a deep trap, where it loses its activity and takes no further part in chemical processes until it finally recombines. However, if the reaction involving the positive ion enables the ion to retain its original activity, the same ion can, of course, take part in a whole series of ion–molecule processes. The most important of these is ionic radiation polymerisation, proposed in order to explain the large yield of polymer in irradiated 2-methylpropene[93,94]. The characteristic features of ionic polymerisation are: a weak temperature dependence of the rate of polymerisation (even a negative temperature coefficient being reported[96]), and a constant molecular weight of the resulting polymer over a wide range of radiation intensities, due to the fact that the lifetime of the chain carriers is independent of the intensity of irradiation. These facts cannot be explained by applying the ideas of the free-radical mechanism of polymerisation, but they fit quite satisfactorily into the conceptual framework of ionic processes[93-95].

The ion R^{+}, leading to polymerisation, can be formed either directly in the primary ionisation event or as a result of an ion–molecule reaction:

$$M \rightsquigarrow R^{+};$$

the chain propagation reactions being

$$R^{+} + M \longrightarrow RM^{+}$$

$$RM_n^{+} + M \longrightarrow RM_{n+1}^{+}.$$

The chain-breaking reactions can take the form of charge transfer

$$RM_n^{+} + M \longrightarrow RM_n + M^{+}$$

or recombination

$$RM_n^{+} + e \rightarrow RM_n.$$

The important role of ions in the polymerisation of 2-methylpropene has been demonstrated by many direct experiments. Thus, it has been shown[94,97,98] that the appearance of free radicals in liquid 2-methylpropene at -78°C does not lead to polymer formation. However, the introduction of positive ions formed in the gas phase into liquid 2-methylpropene causes it to polymerise[99]. The application of an electric field strength of 10^4 V cm^{-1} to 2-methylpropene during irradiation raises the yield of polymer[100] by a factor of 3. This has been ascribed[100] to the greater yield, in an electric field, of free charges which do not recombine with "their own" ions. The reaction is probably initiated by a proton, formed by the primary ionisation act:

$$(CH_3)_2C{=}CH_2 + H^{+} \longrightarrow (CH_3)_2CHCH_2^{+}.$$

The $C_4H_9^{+}$ ion propagates the polymerisation chain. We know also that the $C_4H_9^{+}$ ion is formed in gas-phase ion–molecule reactions when 2-methylpropene is ionised.

The only real proof of the role of ion–molecule reactions in the polymerisation of liquid alkenes was obtained[103,104] in a study of the polymerisation of a mixture of C_2H_4 and C_2D_4. By plotting the mass spectrum of the products of radiation polymerisation (up to C_{18}) it was shown that the number of D atoms in the polymer molecules is invariably a multiple of four. This is evidence that the molecular ions $C_2D_4^{+}$ are taking part in the polymerisation reaction. The reaction itself is apparently of the form

$$C_nH_{2n}^{+} + C_2H_4 \rightarrow C_{n+2}H_{2n+4}^{+}$$

where n = 2, 4, 6, ... The polymerisation chain is broken by the recombination of the ion with an electron. Ionic polymerisation has been recently demonstrated mass-spectrometrically in ethylene in the gas phase, under high pressures[105].

Still further proof of the role of ions in the polymerisation of unsaturated hydrocarbons is the influence of charge-acceptor impurities on the yield of polymers. Thus, addition of ammonia to liquid cyclopentadiene strongly inhibits polymer formation under irradiation [106]. Ammonia undergoes an ion-molecule reaction in pentadiene with proton transfer, giving rise to an NDH_4^+ ion which breaks the polymerisation chain. By measuring the degree of polymerisation as a function of dose in the presence of various concentrations of added ND_3 it was possible to estimate the mean growth time of the chain, equal to the lifetime of the ion, which turned out to be 10^{-3} s for the formation of chains 10^3–10^5 monomer units long. The long lifetime of the ions suggests that only free ions which have escaped recombination can be involved [107]. Of course, shorter-lived ions which have failed to escape from the coulombic interaction with "their own" electron can participate in the formation of shorter chains during polymerisation.

5. Recombination of Ions

The last reaction in which the chemical activity of ions can be utilised is ion recombination. The importance of this process in radiation chemistry was realised from the very earliest radiation-chemical investigations [108,109]. The special features of recombination processes, particularly in the gas phase, have been discussed on many occasions [81,82,110,111]. The recombination of charges results in considerable excitation of one or two molecules, whose ions take part in the process. This excitation can lead to various chemical reactions, such as dissociation or molecular rearrangement, formation of double bonds or cross-links, and so on. The energy evolved in the recombination process depends on the nature of the recombining particles. It is greatest, and equal to the ionisation potential I_M of the molecules, for recombination in the gas phase ($M^+ + e^- \rightarrow M^*$), but it becomes very much less in a condensed phase, particularly when the electron recombining with the positive ion is bound in an electronegative molecule. It should be noted that the energy evolved in recombination in a condensed phase depends essentially on the mode of dissipation of the kinetic energy of the charged particles approaching one another. Thus, if an electron or negative ion, having been captured by the sphere of action of the coulombic field of an ion of the opposite sign, begins to drift towards that ion and move in what is effectively a "viscous" medium, then the energy evolved during the recombination will obviously be

$$E = I_M - \left[\frac{e^2}{\epsilon r} + Q\right],$$

where Q is the electron affinity of the molecule on which the electron is localised before recombination; r is the distance between the charges corresponding to electron transfer rather than drift of the charges in a "viscous" medium. The sum $(e^2/\epsilon r) + Q$ can have quite large values: thus, for $r = 3$ Å and $\epsilon = 2$, $e^2/\epsilon r = 2.5$ eV. The variation of the energy evolved in the recombination with the nature of the negative ion can account for the protective action of various electron-acceptor impurities during radiolysis [83]. If the quantity E is decreased below the level required for dissociation of the molecule, protection becomes possible. This interpretation has been used, for example, in studies of the inhibition by N_2O impurities of the yield of hydrogen in the liquid-phase hydrolysis of saturated hydrocarbons [112]. Since it is known that after capturing an electron N_2O dissociates to form N_2 and O^-, the lower hydrogen yield in the presence of N_2O may be ascribed to the occurrence of the reaction $M^+ + O^-$, which does not produce hydrogen, instead of the reaction $M^+ + e^- \rightarrow H_2$, characteristic of the pure alkane.

Very few papers have dealt with direct experimental studies of the chemical effects of recombination, even in the gas phase [113,114].

The first attempt to identify the products of the recombination process in a condensed phase was made in this laboratory [115,116], relying on the fact that ions and electrons can be made to accumulate when radiolysis is carried out at low temperatures. Recombination can be induced by freeing the charges with light after irradiation, and this is a method for carrying out the ionic reaction under controlled conditions. The effect of visible light on n-heptane irradiated at -196°C is to produce a measurable evolution of hydrogen [115,116], which cannot be explained by assuming that the hydrogen has accumulated in the specimen during irradiation and is freed by the heating effect of the beam of light. We were led to conclude that the hydrogen is formed as molecules in processes such as $M^+ + e^- \rightarrow H_2$ + + double bond, or $M^+ + e^- M \rightarrow H_2$ + cross-linkage.

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The papers discussed in the present review justify the conclusion that the part played by ionised states in radiolysis should not be underestimated. The long lifetimes of ions and electrons in condensed phases allow them to take part in many processes leading to chemical changes in the material.

We are only just beginning to explain the role of ions in various chemical systems under conditions of radiolysis in a condensed phase. Further developments in this field will no doubt advance the state of the art from a rational application of ideas concerning ionic reactions in condensed phases during radiolysis to a general application of these ideas to the interpretation of radiation-chemical processes.

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U.D.C. 543.542:541.48

THE SURFACE TENSION OF MOLTEN SALTS

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I. INTRODUCTION

Molten salts and their mixtures in recent years have been finding ever-increasing application in industry as high-temperature liquids, lubricants, heat-carriers, fluxes, etc. The importance which is being attached to the study of both the bulk and the surface properties of molten salts is thus obvious. Moreover, the study of the physicochemical characteristics of salt melts is a necessary prerequisite for the investigation of the nature of the liquid state and the development of a general theory of liquids.

In view of the vast amount of accumulated information on the physicochemical properties of molten salts in recently published monographs and reviews[1-4] it was impossible to give sufficient attention to each property, including the surface tension of the salts. The increasing interest in experimental data on the surface tension of salts and the non-existence of sufficiently detailed reviews in this field suggest that a review of this type will be opportune and useful.

Before discussing published data on the surface tension of melts, we would point out that we have tried to cover, as completely as possible, papers describing the experimental study of the surface tension of salts and their mixtures; as far as the surface tension of oxide systems is concerned, we have restricted ourselves in the present review to a few papers containing data on the surface tension of the simplest compounds formed in these systems.

II. REVIEW OF EXPERIMENTAL WORK ON THE SURFACE TENSION OF MOLTEN SALTS AND THEIR MIXTURES

The surface tension (σ) of molten salts appears to have been measured for the first time in 1869 by Quinke[5], who used the stationary-drop and drop-weight methods[6-8] to find the capillary constants of melts formed by a number of salts of the alkali and alkaline earth metals. Experimentally, these measurements were unreliable. For example, the temperature of the melts was indefinite, a considerable temperature gradient was unavoidable, and during the measurements there was a danger of decomposition of the melts and contamination from the flame of the heater.

These unsatisfactory features of the determination of σ are also characteristic of the work of Traube[9] and Motylewski[10], who used the drop-weight method find the capillary constants of a large number of inorganic salts.