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Geminate electron–ion pairs generated by ionising radiation in nonpolar hydrocarbon glasses: recombination, polarisation, and separation

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Contents

I. Introduction	383
II. Trapped electrons in solid nonpolar hydrocarbons	384
III. Photo- and thermo-stimulated electron–ion recombination	387
IV. Electric polarisation of electron–ion pairs	390
V. Thermo- and photo-stimulated separation of electron–ion pairs	394

Abstract. Nonpolar hydrocarbons which vitrify at a low temperature constitute a 'classical' model system for the investigation of the characteristic features of the radiolysis of nonpolar organic compounds. Considerable experimental data have now accumulated for hydrocarbon glasses, which permit in many instances quantitative assessments of the applicability of various theories. 3-Methylpentane occupies a special place among these substances. Attention is concentrated mainly in this review on the recombination, polarisation, and separation of the electron–ion pairs generated by ionising radiation. The bibliography includes 163 references.

I. Introduction

The greatest advances in the study of reactions involving excess electrons have been achieved previously for liquid media (see the relevant reviews[1–4]). However, free electrons were first detected in weakly polar glasses. The results of many investigations of liquid and solid hydrocarbons have shown that most of the electrons generated by ionising radiation are thermalised during the interaction with the molecules of the given substance over distances at which the Coulombic potential of the attraction of 'own' positive ions is greater than the thermal energy.[1,5] The charge separation in space depends on the type of ionising radiation. For example, radiation with a low linear density of energy losses (high energy electrons, ^{60}Co γ-radiation, etc.) leads, according to Mozumder,[5,6] to the formation of mainly isolated pairs of charges, in a proportion of 60%–70%. The fraction of pairs forming part of groups containing between 4 and 30 pairs is ~14% while that of pairs in groups with more than 30 pairs is <10%.

The behaviour of 'geminate' pairs of charges (or groups forming a track) is not described by the equations of 'usual' homogeneous kinetics.[7] The unusual feature involving the generation of charged particles on exposure to ionising radiation was noted long ago.[8] At the present time, it has been established that this determines the nature of the kinetics of the ionic processes in the liquid-phase radiolysis of hydrocarbons. Again, this feature must not be disregarded in considering the kinetics of the various phenomena induced by ionising radiation in solid hydrocarbons: isothermal and thermostimulated luminescence, optical absorption, electric conductivity, and photoconductivity.

Extensive experimental data have now accumulated from studies on the behaviour of electrons in solid and liquid nonpolar hydrocarbons. These data indicate the similarity of such systems. The appreciable difference between the time scales of the processes led in the beginning to more active studies on solid hydrocarbons. Certain details of the processes were then elucidated, but these became available to experimenters studying liquid systems only during the last decade. In particular, this applies to the electric polarisation of electron–ion pairs. Many questions concerning the behaviour of electrons in various solid nonpolar media have been answered in a series of review publications (see, for example, Refs 9–12). However, the 'classical' system—vitrifying nonpolar hydro-carbons—still remains under consideration by investigators. This review is devoted to the behaviour of electrons in such a system during processes involving the ionisation, recombination, and separation of electron–ion pairs.

1. Yield of separated pairs of charges

Two very important processes control the kinetics of the reactions involved in the generation of charges by ionising radiation in nonpolar glasses: separation and recombination of electron–ion pairs. The diffusion-drift ideas, based on the consideration of the motion of classical particles with a mean free path much shorter than the characteristic dimension of the problem, are usually employed to describe these processes in an amorphous nonpolar substance.[13,14] The simplest case is that of isolated pairs.

Having applied the Smołuchowski equation to this case, Onsager[15] obtained the exact expression for the probability $\phi(\boldsymbol{r},\boldsymbol{E})$ of the separation of charged particles, the position of which is specified by the vector $\boldsymbol{r}$ directed at an angle θ relative to the external field $\boldsymbol{E}$ with a strength E (Fig. 1).

$$\phi(\boldsymbol{r},\boldsymbol{E}) = \exp\left[-\frac{r_c}{r} - \beta r(1+\cos\theta)\right] \times \sum_{m,n=0}^{\infty} \frac{\beta^{n+m}(1+\cos\theta)^{n+m} r_c^m r^n}{m!(m+n)!} \quad (1)$$

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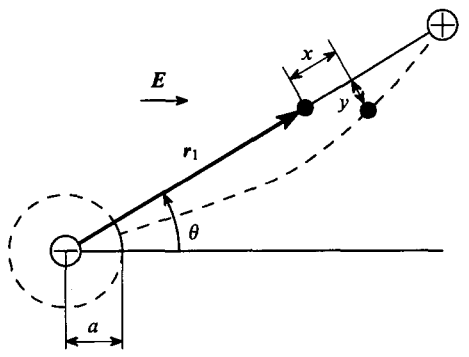


Figure 1. Schematic explanation of the notation. The radius vector of the electron in the absence of an external field is r_1; the trajectory in the mutual approach of ions without allowance for diffusion in the presence of an external field E is shown dashed; x and y are respectively the radial and tangential deviations of the position of the electron from r_1 in the presence of an external field.

After averaging with respect to the angle θ, we have[16]

$$\phi(r,E) = 1 - (2\beta r)^{-1} \sum_{m=1}^{\infty} P(m,2\beta r) P\left(m,\frac{r_c}{r}\right) , \qquad (2)$$

where

$$\beta = \frac{eE}{2k_B T}, \quad P(m,x) = [(m-1)!]^{-1} \int_0^x \exp(-t) t^{m-1} dr .$$

For $E = 0$, Eqn (1), known as the Onsager formula, reduces to

$$\phi_0 = \exp\left(-\frac{r_c}{r}\right) , \qquad (3)$$

where r_c, given by

$$r_c = \frac{e^2}{\varepsilon k_B T} ,$$

is the so called Onsager radius, ε is the relative permittivity, k_B is the Boltzmann constant, and e is the charge on the electron. According to Mozumder,[17] the Onsager model can be used also for electron–ion pairs generated by ionising radiation.

On this hypothesis, it is possible to relate the initial distribution function of thermalised electrons $F(r)$ to the yield $G_{fi}(E)$ of the separated pairs of charges (or the number of separated pairs per unit ionising radiation energy absorbed by the substance):

$$G_{fi}(E) = G_0 \int_0^{\infty} F(r)\,\phi(r,E) dr , \qquad (4)$$

where G_0 is the overall initial yield of the pairs of charges. Eqn (4) makes it possible to infer from the experimental data for G_{fi} the distribution function of the thermalised electrons. This approach has been hitherto one of the important sources of information about $F(r)$.[18,19]

For many liquids, the experimental $G_{fi}(E)$ data were obtained as early as the 1970s, mainly with the aid of electrical methods based on the measurement of the number of charges drawn by the electric field onto the electrodes under conditions preventing the influence of bulk-phase recombination (see, for example, Freeman[20] and Schiller and Vass[21]). The yield in a zero field $G_{fi}(0)$ may be found by extrapolating the $G_{fi}(E)$ relation to $E = 0$. Another, more reliable method for the estimation of $G_{fi}(0)$ involves the use of the cleaning field method.[22] In this method, the electric field withdrawing charges onto electrodes is applied after a short electron–ion pair generation pulse for a period sufficient to complete pair recombination.

Until recently, experimental G_{fi} data referred almost exclusively to liquid dielectric materials. For solid amorphous substances, the determination of G_{fi} by the method involving the withdrawal of charged species is handicapped by the fact that the mobility of such species is as a rule very low. G_{fi} data for solid organic glasses were obtained much later.

2. The spatial distribution function of thermalised electrons

The form of $F(r)$ is difficult to determine from experimental $G_{fi}(E)$ data and Eqn (4). For practical purposes, some kind of simple form of the $F(r)$ relation is normally employed.[1,13] In the analysis of experimental data for liquids, most attention has been devoted to the following types of distribution:

simple exponential:[23]

$$F(r) = C\exp\left(-\frac{r}{b}\right) , \qquad (5)$$

Gaussian:[24]

$$F(r) = Cr^2 \exp\left(-\frac{r^2}{b^2}\right) , \qquad (6)$$

amplified Gaussian:[25]

$$F(r) = \begin{cases} Cr^2 \exp\left(-\dfrac{r^2}{b^2}\right) & r < 2.4b , \\ Cr^2 \exp\left(-\dfrac{r^2}{b^2}\right) + 0.5\left(\dfrac{b^2}{r^2}\right) & r > 2.4b . \end{cases} \qquad (7)$$

Here C is the normalising multiplier and b the parameter of the distribution function.

Apart from Eqns (5)–(7), others have also been tested: the delta-function, the Gaussian relation with a displaced maximum, etc. Among these relations, functions (5) and (7) yielded the most satisfactory agreement with experimental data for $G_{fi}(E)$.[13,18,19,26]

Estimates based on Eqn (4) and G_{fi} data for different liquids yield approximately identical values of b for functions (5) and (7). In the case of unbranched hydrocarbons, the values of parameter b are in the range 50–70 Å,[20–26] which indicates a fairly narrow (compared with the Onsager radius) distribution of the thermalised electrons.

In order to compare the paths traversed by superthermal electrons in various substances, it is convenient to employ the values of b normalised with respect to density (or the product $b\rho$, where ρ is the density of the substance). The values of $b\rho$ in liquid hydrocarbons (in contrast to gases) are independent of ρ and depend only slightly on the temperature of the substance.[18,19]

II. Trapped electrons in solid nonpolar hydrocarbons

1. Detection of a trapped electron

The study of trapped (stabilised) electrons e_{tr}^- in solid hydrocarbons was initiated long ago. The first attempts to detect e_{tr}^-, undertaken in 1962,[27] did not lead to positive results. Subsequently, using an improved technique for the measurement of the optical absorption spectra in frozen hydrocarbons γ-irradiated at 77 K, it was possible to observe an absorption band in 3-methylpentane,[28] extremely sensitive to 'bleaching' by IR light, the maximum of which was at a much higher wavelength than the absorption band of a trapped electron in alcohols with a relatively low IR sensitivity.

Later a broad ($\Delta E_{1/2} \approx 0.5$ eV) structureless optical absorption band with a maximum in the range 1500 to 2000 nm was observed in the spectra of other substances: on radiolysis of alkane

and olefin glasses and also on UV irradiation of substances with a low ionisation potential or containing the anions of aromatic hydrocarbons in alkane glasses as additives. This absorption, attributed in all cases to trapped electrons, is readily bleached by visible and by near IR irradiation within the limits of the absorption band, disappearing gradually in the dark even at 77 K.[12]

The use of electron-accepting additives is of decisive importance for the identification of the optical absorption bands in the near infrared in irradiated hydrocarbons at a low temperature. In their presence, the intensity of the optical absorption diminishes with the simultaneous formation of the radical-anions of the additive, which have been reliably identified from the known optical absorption or EPR spectra.

The concentration of electrons stabilised in hydrocarbons decreases also in the presence of substances reacting with slow electrons via a dissociative capture mechanism (alkyl halides, esters, etc.). On the other hand, the addition of positive charge acceptors (olefins, alcohols, ethers, aromatic amines) increases the radiation yield of the stabilised charges. All these data as well as the presence of a narrow signal in the EPR spectra[29] permitted the conclusion that the optical absorption band in the near infrared in the irradiated hydrocarbons is due to trapped electrons.[12]

On exposure to light or with increase in the temperature of the specimen, the electrons stabilised in the irradiated specimens are liberated. In the presence of an acceptor, this entails an increase in the concentration of the radical-anions, since the electrons leaving the traps are captured by the additive.[30] After successive illumination of the specimens, Gallivan and Hamill[31] observed reversible electron transfer between the 3-methylpentane and added biphenyl from the absorption spectra at wavelengths corresponding to the absorption bands of e_{tr}^- and the biphenyl radical-anion. The molar absorption coefficient of the trapped electron (λ = 1600 nm) $\epsilon(e_{tr}^-) = 3 \times 10^4$ litre mol^{-1} cm^{-1} was first determined from these data. From this value, the radiation yield G_{tr} of the trapped electrons in 3-methylpentane was found.[31,32] Immediately after γ-irradiation at 77 K, G_{tr} was ~0.8, but this value diminishes rapidly with increase in the dose. The estimated $\epsilon(e_{tr}^-)$ agrees to within 25% with the estimate of 4×10^4 litre mol^{-1} cm^{-1} (for λ = 1600 nm) based on the EPR spectrum.[29] The values of $\epsilon(e_{tr}^-)$ for the majority of saturated hydrocarbons are similar.[31,33–35]

2. The nature of the optical absorption of the trapped electron

In the first studies[32] on γ-irradiated alkanes at 77 K, it was found that the quantum yield φ of the photobleaching of e_{tr}^- is ~0.8 for λ = 950 nm, ~0.4 for λ = 1300–1600 nm, and 10^{-2} for λ > 1700 nm. The low quantum yield for the long-wavelength absorption edge of e_{tr}^- is caused, according to Hamill,[36] by the transition to the bound state at λ > 1700 nm, while $\varphi \approx 1$ for the short-wavelength edge is due to the transition to a continuum with formation of a mobile electron e_m^-:

$$e_{tr}^- + h\nu \rightarrow e_m^- \quad . \tag{8}$$

A more detailed study of this relation for the range 1300 < λ < 2150 nm in 3-methylpentane was undertaken by Miller and Willard,[37] who observed that φ(1800 nm) = 0.7 φ(1600 nm) and φ(2000 nm) = 0.2 φ(1600 nm). Some photobleaching at $\lambda \approx$ 2150 nm was also noted, while at λ > 2300 nm photobleaching was not observed. The decrease in φ with increase in λ in the region $\lambda > \lambda_{max}$ could not be induced by the transition to a bound state in the trap but might be caused by the recapture of electrons[37] or the absorption of light by the hydrocarbon molecules.[38]

The dependence of the induced photoconductivity current on the wavelength $I_{ph}(\lambda)$ was later used to obtain the similar dependence of the number of photoionisation steps per absorbed photon $\beta'(\lambda)$†.[39] This is a more direct method for the study of the photoionisation of e_{tr}^- than photobleaching and recombination luminescence. It was found by this procedure[39] that $\beta'(\lambda) \approx$ const for λ < 1150 nm in 3-methylhexanes; the decrease in the photocurrent in the region λ > 1150 nm was attributed to[39] the decrease in $\beta'(\lambda)$. Narrow 'dips' in the induced photoconductivity spectra of γ-irradiated isooctane, cyclohexane, methylcyclohexane, and 3-methylpentane have been observed;[39,40] a correspondence between the dips in the spectra and the overtone absorption of the hydrocarbon matrices was established.

The slight 'temperature-induced' changes in the form of the absorption spectra of e_{tr}^- in the long-wavelength region (a hypsochromic shift) have been observed for 3-methylpentane at a constant temperature (T = 76 K) at time intervals from milliseconds to minutes[41] and also on varying the irradiation temperature of 3-methylpentane (in the range from 4 to 73 K[35] and from 77 to 110 K[42,43]) and on annealing the specimen before irradiation.[44]

The available literature data, based mainly on spectroscopic measurements, permit the following conclusions:

1. The decrease in the intensity of the absorption of light by e_{tr}^- observed following the introduction of acceptor additives, on isothermal decay, on photobleaching, and after annealing the specimens before irradiation, accompanied by significant changes in the form of the optical absorption band of e_{tr}^-, indicates the stabilisation of electrons in traps of the same nature.

2. Integration of the absorption band of e_{tr}^- yields the oscillator strength $f \approx 1$. This quantity is characteristic of the 'initial' absorption spectra of e_{tr}^- in alkane glasses.[31,34,35,45]

3. The broad structureless absorption band of e_{tr}^- cannot be fully caused by optical transitions to the bound state. At least its short-wavelength edge is due to the transition to a continuous spectrum with a quantum yield close to unity.[30,32,37,40,41,46–54]

The problem of the nature of the optical absorption of e_{tr}^- in nonpolar hydrocarbons — transition to a bound state in a trap or transition to a continuum — has still not been solved.[53] Both views have been maintained in numerous publications. In particular, it has been suggested that detailed comparison of the spectra of the induced photoconductivity and the induced optical absorption in optical glasses would make it possible to separate these transitions for trapped electrons.[30,40,50–52,54] For example, it is assumed that, for transitions to a continuous spectrum, the photoconductivity spectra should be superimposed on the optical absorption spectra.[49] However, this conclusion is evident only for free electrons.[53] The characteristic features of the contributions to the photoconductivity by bound and free electrons are discussed below.

a. The nature of electron traps

The molecules of saturated hydrocarbons have no electron affinity in the ground state. It is natural to expect that in the solid phase for low irradiation doses the physical inhomogeneities in the matrix serve as electron traps.[55,56] This is indicated by the following facts: (1) the dependence of the recombination luminescence and the electrical conductivity induced by the ionising radiation on the degree of crystallinity of the specimen; (2) the influence of preliminary annealing of the 3-methylpentane glass at 77 K on the yield of stabilised electrons; (3) the continuous variation of the optical spectra of stabilised electrons in irradiated glasses following the addition of another glass-forming component.

For large irradiation doses, free radicals, which may serve as electron traps, accumulate in low-molecular-mass hydrocarbons.[57,58] An estimate of the radius of the reaction involving electron capture by a radical from measurements of the induced photoconductivity[59] and of the thermostimulated current in γ-irradiated 3-methylpentane yielded the following value:[60]

$$R_r = \frac{k_R}{4\pi D} = 15 \pm 3\,\text{Å} \ ,$$

where k_R is the constant for the trapping of the electron by the radical, and D is the diffusion coefficient.

† It is necessary to distinguish the quantities $\beta'(\lambda)$ and $\varphi(\lambda)$. The latter decreases, according to Skelly and Hamill,[32] during the bleaching of e_{tr}^-.

Data for the concentrations of traps in hydrocarbons have been obtained largely by the method of competing electron-accepting additives. The concentrations of the traps estimated in studies by different workers vary within wide limits—from 10^{16} to 10^{20} cm^{-3}. Reversible electron transfer between the traps in methylcyclohexane and 3-methylpentane matrices (specially freed from electron acceptors) and the added pyrene and also between traps in isooctane and isooctane free radicals has been observed on the basis of induced photoconductivity spectra.[30] These investigations led to the following concentrations of traps (in cm^{-3}): 1×10^{18} for 3-methylpentane, 3×10^{17} for methylcyclohexane, and 1×10^{15} for isooctane.

The first estimate of the depth of electron traps was probably made for 3-methylpentane and amounted to 0.09 eV.[31] The same depth of traps was found in early studies on recombination luminescence at 77 K; traps with energies of 0.1 and 0.25 eV have been detected in 3-methylpentane[61,62] and traps with energies of 0.18 and 0.21 eV have been found in n-heptane.[63] Relatively small depths of electron traps in hydrocarbon glasses are characteristic of the early investigations. In later studies, the authors of which used many fewer substances and applied better founded theoretical models, greater depths were found. For example, an activation energy of 0.65 ± 0.05 eV has been obtained from the analysis of the form of the radiothermoluminescence peak of specially pure γ-irradiated 3-methylpentane.[64] This result agrees with data obtained in other investigations[65,66] (the temperature jump method). In order to account for the great depth found for the traps, the authors of these studies suggested that the molecular rearrangement of the hydrocarbon matrix plays a significant role in the thermal liberation of an electron.

Fig. 2 presents the temperature dependence of the drift mobility μ_d of an electron in 3-methylpentane.[67] Evidently, in the temperature range 94–296 K, the value of μ_d changes by more than eight orders of magnitude when account is taken solely of data obtained by the direct method. When account is taken of the estimate for 77 K (the lifetime of the electron in the trap is $\tau_{77} \approx 1.5 \times 10^3$ s[68]), the changes in μ_d are by more than fourteen orders of magnitude. On the $\mu_d(1/T)$ relation, it is possible to distinguish two temperature ranges to which activation energies of ~0.14 and ~0.4 eV correspond; the boundary between them corresponds approximately to the melting point of 3-methylpentane. The form of the $G_{fi}(1/T)$ relation changes sharply in the same temperature range.

The activation energies for nondeuteriated and deuteriated amorphous methylcyclohexane have been found from the initial sections of the low-temperature radiothermoluminescence and thermostimulated current peaks. At 92 K, they amounted to 0.32 ± 0.05 and 0.37 ± 0.08 eV in the former case and 0.34 ± 0.05 and 0.38 ± 0.08 eV in the latter.[69]

Estimates of the minimum depth of traps from the threshold of the photoabstraction of an electron from the e_{tr}^- state lead to somewhat higher energies than in the thermal liberation of electrons from traps. Thus the following estimates have been obtained for the minimum energy of the light quantum necessary to liberate an electron in 3-methylpentane (eV): 0.7,[32,36] 0.53,[37] 0.37,[46] and 0.62.[51] Data concerning the influence of IR irradiation on the yield of free charges and 3-methylpentane are best explained for a photoabstraction threshold of 0.5 eV.[70] For methylcyclohexane, the results of experiments designed to investigate the influence of photobleaching on the initial induced photoconductivity spectra have shown that 80% of the traps have an electron photoabstraction energy in the range 0.44–0.62 eV.[40] It may be that the smaller photo- and thermal-abstraction energies correspond to the e_{tr}^- in 'closer' pairs. The observed higher electron photoabstraction energies compared with the thermal abstraction are usually attributed, in most investigations, to the fact that the photoabstraction of an electron takes place in conformity with the Franck–Condon principle.

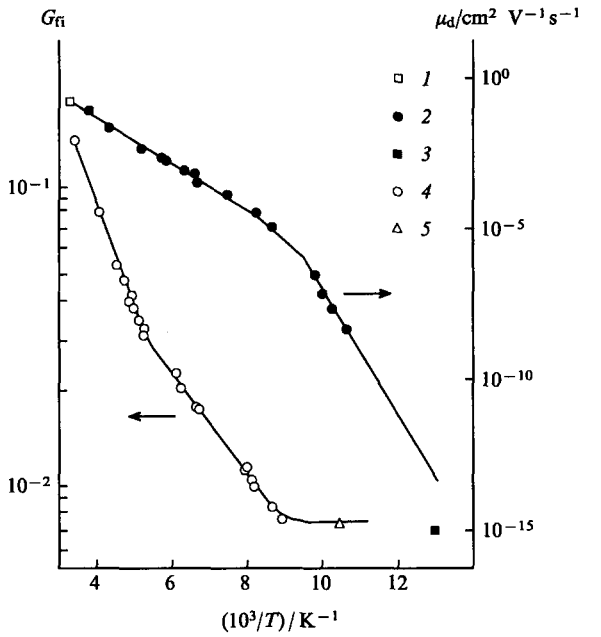


Figure 2. Temperature dependence of the radiation yield G_{fi} (1/100 eV) and of the drift mobility μ_d of electrons in 3-methylpentane.[67] The results were obtained by different methods: (*1*) from the time of flight and the conductivity amplitude; (*2*) from the conductivity amplitude; (*3*) calculation of the mobility based on the quantity $G\mu_0\tau_0$ for ^{60}Co γ-irradiation and of the lifetime of the electron in the trap τ_{77}; (*4*) from the range of conductivity currents; (*5*) from the integration of the thermostimulated current peak.

b. 'Polaron' and 'nonpolaron' models of a trapped electron

Theoretical models of trapped electrons in hydrocarbon glasses have been discussed frequently (see, for example, the relevant reviews[12,56]), but so far there is no reliable model. Despite the fact that this topic is not the main one under consideration in the present review, we shall make several comments.

One might postulate that, when a thermalised electron enters the stabilisation region, a potential well arises as a result of the polarisation of the surrounding molecules and one should consider a model analogous to the polarised cavity model for polar substances.[71] However, soon after the detection of e_{tr}^- it was noted[72] that the polaron model is not applicable to the description of the localised state of an electron in nonpolar substances; the total energy of the electron in the polaron model can be formulated as follows:

$$E' \propto \frac{h^2}{8mr^2} - \frac{e^2}{r}\left(\frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_0}\right), \qquad (9)$$

where the first term on the right-hand side is the kinetic energy of an electron bounded by a sphere with a radius r and an infinite potential barrier and m is the mass of the electron; the second term represents the attraction energy, while ε_∞ and ε_0 are the optical and static relative permittivities. In polar media, the difference between ε_∞ and ε_0 is fairly large, so that the second term in Eqn (9) is greater than the first. In nonpolar media, ε_∞ and ε_0 differ only by the contribution of the atomic polarisation, which does not exceed 5%–10% of ε_∞.

The experimental band of e_{tr}^- is narrower than the band for the dependence of the cross-section for the photoabstraction of an electron from H^- on the energy[73] when the latter is recalculated for $\lambda_{max} = 1600$ nm.[46] For a theoretical description of the form of the e_{tr}^- spectrum, the form of the potential of the trap has been varied[45] using the hydrogen-like atom model. Best agreement with experiment was achieved in a calculation on the assumption that the absorption spectrum of e_{tr}^- is due to the

transition to a continuum. The required form of the potential of the trap proved to be more 'rectangular' than in the case of a Coulombic well. The first attempt to relate the absorption spectrum of e_{tr}^- to the structure of the frozen hydrocarbon was apparently made in the paper of Funabashi and Maruyama.[74] These workers indicated the possibility, in principle, of describing the form of the e_{tr}^- spectrum in both visible and IR regions on the assumption that the traps in solid hydrocarbons consist of regions with a nonordered arrangement of the molecules.

The results of the majority of studies indicate that regions with a low density (cavities) serve as traps in alkanes.[56] This agrees with the 'bubble' model, which has been used successfully to describe the properties of the localised state of an electron in liquefied and solid noble gases,[75] which also have no electron affinity in the gas phase. The stability criterion obtained when this model is extended to solid hydrocarbons[72] differs from that found in the case of the polaron model:

$$\frac{h^2}{8mr^2} - \frac{n'e^2\alpha_0 4}{2r} \leq V_0 \ , \qquad (10)$$

where the second term on the left-hand side takes into account the energy of electronic polarisation (n' is the density of the substance for r greater than the radius of the cavity, and α_0 is the polarisability), while V_0 is the energy level of the quasi-free state of an electron in the given substance relative to the level in vacuo. In contrast to Eqn (9), the criterion specified by Eqn (10) satisfied reasonable values of V_0, α_0, and r.[72]

According to the results[76] for deuteriated 3-methylpentane (77 K, spin echo), the contribution to the stabilisation of the electron comes not only from the dipoles of the C–H bonds of the neighbouring molecules, as postulated previously, but also from the polarisability of the C–C bonds. A satisfactory agreement between the calculation within the framework of the 'bubble' model (potential well with vertical walls) and the initial experimental photoionisation spectrum of e_{tr}^- in methylcyclohexane has been achieved for a cavity radius of 3.73–3.85 Å and a photoionisation threshold of 0.40–0.44 eV.[40]

III. Photo- and thermo-stimulated electron–ion recombination

Studies on the radiation-induced luminescence should apparently be regarded as the initial experimental data which determine the direction adopted in the investigation of the recombination of geminal electron–ion pairs in nonpolar glasses. This method made it possible to observe the changes in the rate of recombination over a wide dynamic range.

1. Studies on recombination luminescence

A prolonged afterglow (half-life $\tau_{1/2}$ = 5–20 min at 77 K)—isothermal luminescence (IL)—has been noted in solid saturated,[77] unsaturated,[78] and aromatic[79] hydrocarbons subjected to the action of ionising radiation. After its decay, a new flash of luminescence may be induced by a rise in temperature—radiothermoluminescence (RTL)—or by illumination by light at wavelengths corresponding to the region in which e_{tr}^- absorbs—radiophotoluminescence (RPL).

It had already been established in early studies that the kinetics of the decay of the isothermal luminescence $L^*(t)$[46,80] and of the optical density of the trapped electron $D(t)$[31,32,80] are inconsistent with either first- or second-order kinetics for the process and cannot be expressed in terms of their combination. Joint studies on the decay of $D(t)$ and $L^*(t)$ showed[32,80] that the optical density and the intensity of isothermal luminescence are linked by the relation

$$\int_0^t L^*(t)\mathrm{d}t \propto D^0 - D(t) \ , \qquad (11)$$

where D^0 is the initial optical density of e_{tr}^- at $t = 0$.

The decay of $D(t)$ and $L^*(t)$ in solid nonpolar hydrocarbons is independent of the irradiation dose. In many cases the decay of $L^*(t)$ can be described by the relation[78]

$$\frac{L_0^*}{L^*(t)} = 1 + \varrho(t - t_0) \ , \qquad (12)$$

(ϱ is a constant and t_0 the time at the start of the observation), formally corresponding to a second-order reaction. However, since ϱ is independent of the irradiation dose, it follows that $L^*(t)$ is not determined by the average concentration of charges in the bulk of the substance and in this sense the decay law (12) corresponds to a pseudo first-order reaction.[81]

Pure hydrocarbons give rise to a weak RTL. Typical RTL curves consist of several peaks (for example, two peaks at $T_1 \approx 81$ K and $T_2 \approx 85$ K for 3-methylpentane[32,82–86]). The luminescence intensifies after the addition of electron acceptors[85,86] and both monomeric and dimeric luminescence due to the added acceptor is then observed (in conformity with studies on the luminescence arising on excitation of liquid solutions by ionising radiation[87]).

If the γ-irradiated specimens are bleached by IR light before heating, the low-temperature peaks are suppressed. This fact has been attributed to the recombination of the electrons e_{tr}^- liberated by light from the traps.[32,82] Together with this effect, a sharp increase in the RTL intensity was observed at higher temperatures and for low irradiation doses in specially pure substances, which was manifested by the appearance of new peaks.[84–86] The new RTL peaks are not associated with geminate recombination but are due to the recombination of free ions, the irradiation yield of which increases on photostimulated (in contrast to thermostimulated) separation of the geminate pairs.

With increase in the γ-irradiation dose (for example, from 5×10^2 to 3×10^4 rad for 3-methylpentane),[64] the form of the RTL peaks does not change and their intensity remains proportional to the dose. Such a dose dependence is usual for RTL in organic dielectric materials[88–90] and has been attributed to the pair recombination mechanism.

The difference between the RTL curves for the specimens unbleached and bleached by IR light initially increases sharply during bleaching and then reaches saturation (for 3-methylpentane in the range from 10^2 to 10^3 in units of $\sigma_{ph}Lt$, where σ_{ph} is the photoionisation cross-section and L is the light intensity). The decay of the RPL by a factor greater than 10^3 has been observed in 3-methylpentane at 77 K.[64,91] The integral RTL_{bl} intensity agrees with the integral RPL intensity during IR illumination (this has been tested for 3-methylpentane as far as the decrease in the RPL by a factor of 400).[64]

2. The problem of the kinetics of the thermo- and photo-stimulated electron–ion recombination

In the analysis of experimental data on the kinetics of inhomogeneous processes in liquid hydrocarbons (geminate recombination, the trapping of an electron from a geminate pair by an acceptor, separation of the pair), both deterministic and stochastic approaches are used nowadays to equal extents (see, for example, the relevant review publications[7,13,92,93]). No examples of the analysis of data within the framework of the stochastic approach are known for solid hydrocarbons (including numerical calculations by the Monte Carlo methods).

Two types of processes differing appreciably in time have been differentiated in solid hydrocarbons: (1) recombination of quasi-free electrons which had never been captured by traps before recombination; (2) comparatively slow recombination of electrons which had been captured by a trap at least once. The recombination of the first type proceeds with a characteristic time $t \approx \varepsilon b^3/3\mu_0 e \approx 10^{-13}$–$10^{-9}$ s, where b is the thermalisation length and μ_0 the mobility of the quasi-free electrons.[94] The characteristic time of the recombination of the second type is determined by the lifetime of the electron in the localised state and

for systems at a low temperature can attain considerable durations (minutes and hours). Almost all the experimental studies on the kinetics of recombination in solid amorphous substances have been devoted to this particular type of recombination.

A general approach to the description of the kinetics of the pair recombination of e_{tr}^- and a positive ion M^+ must take into account three factors: firstly, the distribution with respect to distances in the pair $\{e_{tr}^-, M^+\}$; secondly, the distribution of e_{tr}^- with respect to the depth of the traps; thirdly, the possibility of transcapture, i.e. of the transfer of an electron from one trap to another. The case of recombination where it is possible to disregard the last factor is easiest for the description of the kinetics. In such recombination, the electron passes from the localised state e_{tr}^- to M^+ without being captured by another trap. The transition can occur either as a result of a tunnelling process or via the photo- or thermo-abstraction of an electron from the trap. Regardless of the mechanism of the transition, the problem reduces to the summation of the rates of unimolecular reactions occurring with different characteristic times.[95,96]

We shall consider the proportion of e_{tr}^- recombining without transcapture. For photostimulated recombinations, an answer to this question is provided by measurement of the quantum yield φ of the bleaching of e_{tr}^-. According to the data of Skelly and Hamill[32] and Oka et al.,[97] φ for irradiated 3-methylpentane glass diminishes in the course of bleaching from 0.4–0.8 to zero. These data show that a considerable proportion (40%–80%) but by no means all the captured electrons recombine without transcapture. This fraction includes mainly electrons located at short distances from M^+.

Allowance for the other part of the e_{tr}^-, recombining as a result of one or several transitions between traps, appears important for the analysis of the kinetics of various phenomena.[98] This part is in fact mainly responsible for the trapping of electrons by acceptor molecules at relatively low concentrations and also for the postradiative change in the electrical and optical properties of dielectric substances.

The solution of Smŏjuchowski's equation in the form proposed by Ichikawa et al.[99] has been used to describe the kinetics of the recombination of such pairs in studies[83] of the isothermal luminescence of 3-methylpentane at 77 K:

$$\frac{1}{D_0}\frac{\partial W(r,\tau)}{\partial \tau} = \frac{\partial^2 W(r,\tau)}{\partial r^2} + \left(\frac{2}{r}+\frac{r_c}{r^2}\right)\frac{\partial W(r,\tau)}{\partial r}\ , \qquad (13)$$

where $\tau = t/t_{1/2}$ is dimensionless time, $t_{1/2}$ the half-life of the luminescence, $D_0 = Dt_{1/2}$ the temperature-independent diffusion coefficient, and $W(r,\tau)$ the probability of observing the electron at time τ at a distance r from the cation. Having expressed the time variation of the luminescence intensity $L^*(t)$ as the sum of the exponential functions,

$$L^* = \sum a_i \exp(-k_i\tau) \qquad (14)$$

(a_i and k_i are coefficients), with the aid of the substitution $W(r,\tau) = \sum R_i \exp(-k_i\tau)$, Eqn (13) can be reduced to a system of ordinary differential equations:

$$\frac{d^2R_i(r)}{dr^2} + \left(\frac{2}{r}+\frac{r_c}{r^2}\right)\frac{dR_i(r)}{dr} + \frac{k_i}{D_0}R_i(r) = 0\ , \qquad (15)$$

subject to the conditions $[R_i(r)]_{r=r_0} = 0$ and $[dR_i(r)/dr]_{r=r_0} = k_i a_i/4\pi r_0^2 D_0$. After adjusting the calculated experimental data for consistency, a half-life of 140 s and an electron diffusion coefficient of $\sim 10^{-13}$ cm^2 s^{-1} were obtained[83] at 77 K.

The use of the concept of the diffusion of classical species for the description of the pair recombination in solid amorphous substances cannot be justified in the general case, since the diffusion of the species is strongly hindered in this case: an appreciable proportion of the electrons are stabilised in traps, forming a comparatively long-lived e_{tr}^- state. Discrepancies between the diffusion theory and experiment may be expected in the early stages of the electron–ion recombination.[100]

The tunnelling mechanism of the recombination has been reliably established for glasses at $T \sim 4$ K and also for hard hydrocarbon glasses (of the type of methylcyclohexane) at higher temperatures (see, for example, the relevant reviews[95,96]). The conclusion that such a mechanism operates has been based on the weak temperature dependence of the rate of decay of the isothermal recombination luminescence or on the concentration of the radical-ions detected by optical or EPR methods. The concentration dependence, which can be expressed in a linear form by plotting the concentration against lg t, is characteristic of the tunnelling mechanism.[101] Such a dependence corresponds to a decrease in the intensity of the recombination luminescence in accordance with the law defined by Eqn (12).

As in the case of the reactions of heavy particles,[102] the dominant role of the tunnelling mechanism of recombination is to be expected at low temperatures and for short distances between the reacting particles. With increase in the temperature of the medium or in the distance between the reacting particles, the role of transitions over the barrier should increase. The temperature at which the effectiveness of these processes becomes equal can be estimated from the relation[103]

$$\tilde{T} = \frac{\hbar}{\pi k_B l}\sqrt{\frac{\Delta E}{2m}}\ , \qquad (16)$$

where l is the distance between the reacting species, and ΔE is the height of the tunnelling barrier or the difference between the energies of the ground states of the quasi-free and trapped electrons.

According to Eqns (16), the predominance of the activation mechanism in the electron–ion recombination may be expected in nonpolar hydrocarbons at $\tilde{T} \geqslant 100$ K. This agrees with the estimate[101] of the typical average distance (40–50 Å) between the anion and the cation in a nonpolar medium, whereupon the tunnelling mechanism of the reactions begins to predominate. One of the examples of the thermoactivated recombination is provided by the electron–ion recombination in the 3-methylpentane glass at $\tilde{T} \geqslant 70$ K.[66,83,104]

3. The distribution function of the pairs with respect to the number of electron transitions between traps before recombination

It is frequently convenient to divide charges arbitrarily into two groups—bound or geminate and free—depending on whether they recombine with positive ions in their own or another track respectively, and the rate of recombination can be written in the form[64,68,91,105]

$$W_r(t) = W_g(t) + W_{fi}(t)\ . \qquad (17)$$

The term $W_g(t)$—the rate of recombination of bound charges—should correspond to a pseudo first order of the reaction according to numerous experimental data.

The recombination of free charges can be described by the equations of normal homogeneous kinetics, whereupon

$$W_{fi} = k_r \bar{n}_+ \bar{n}_-\ , \qquad (18)$$

where $\bar{n}_+$ and $\bar{n}_-$ are the average concentrations of the positive and negative charges and k_r is the recombination reaction rate constant.

We shall consider a simple model taking into account the electron recapture.[68,105] In the analysis of the kinetics of the recombination, we shall take into account only that part of $W_r(t)$ which is associated with the recombination of electrons which have been captured by traps. We shall assume that only one current carrier (an electron) is mobile and that the contribution of the tunnelling transitions to the rate of the recombination reaction is negligible compared with the thermal liberation of the electrons from traps.

One can then write for the rate of the recombination reaction

$$W_r(t) \propto \sum_{N=1}^{\infty} Y(N)\, \omega_N(t)\left(\frac{1}{\tau}\right) , \qquad (19)$$

where $Y(N)$ is the initial distribution function for electrons with respect to the number of captures N by traps before recombination, ω_N is the probability that the electron executes $N-1$ transitions between traps at time t, τ is the lifetime of the electron in the trap equal, for example, to $(\sigma_{ph}L)^{-1}$ on photoliberation, σ_{ph} is the photoionisation cross-section, and L is the light intensity.

The functions $\omega_N(t)$ satisfy the equations

$$\frac{d\omega_1}{dt} = -\frac{1}{\tau}\omega_1 , \qquad \frac{d\omega_{i>1}}{dt} = \frac{1}{\tau}(-\omega_i + \omega_{i-1}) , \qquad (20)$$

and the initial conditions

$$\omega_{i=1}(t=0) = 1 , \qquad \omega_{i>1}(t=0) = 0 .$$

The Poisson function

$$\omega_N(x) = \frac{(x)^{N-1}}{(N-1)!}e^{-x} , \qquad (21)$$

where

$$x = \int_0^t \frac{dt}{\tau} ,$$

is a solution of Eqn (20). The type (21) functions $\omega_N(x)$ are normalised with respect to unity and have a maximum at $x = N-1$ with a width at half the height $\Delta_{1/2} \approx \sqrt{N}$ for $N \gg 1$.

When account is taken of the number of light quanta corresponding to one recombination step, Eqns (19) and (21) make it possible to find the relation $L^*(t) \propto W(t)$ for the recombination luminescence when the functions $Y(N)$ and $\tau(t)$ are known.

a. The lifetime of the electron in the trap. Data on the distribution $Y(N)$

Since the optical absorption of e_{tr}^- at $\lambda = 1000$ nm leads to the liberation of the electron from the trap with a quantum yield $\beta \approx 1$ (see Section II.2), the characteristic lifetime of the electron in the trap during bleaching can be expressed as follows:

$$\tau_b^{-1} = \sigma_{ph}L + \tau_{77}^{-1} ,$$

where τ_{77} is the 'dark' lifetime ($L = 0$, $T = 77$ K). It follows from Eqn (19) that, for example, for RPL,

$$\frac{L^*}{L} \propto \sum_{N=1}^{\infty} Y(N)\omega_N(x) , \qquad x = \int_0^t \sigma_{ph}L\, dt . \qquad (22)$$

Using Eqn (22) and the data for the decay of RPL, one can obtain information about the distribution $Y(N)$ when account is taken of the thermal liberation of the electron from the trap during the period from the instant of generation to the beginning of the IR illumination:

$$x_0 = \frac{0.5\Delta t_\gamma + \Delta t_{77}}{\tau_{77}} ,$$

where Δt_γ is the duration of the γ-irradiation and Δt_{77} the time after the cessation of irradiation and before the start of illumination. Such an estimate yielded $\tau_{77} = 20-35$ min.[64] Analysis of literature data,[31,32,46,80] carried out by the present authors,[68] also led to a similar value of τ_{77} ($\approx 26.5 \pm 3$ min). A satisfactory agreement with experiment has been achieved[64,91] for the distribution function

$$Y(N) = \begin{cases} 2.5 & N = 1 ; \\ N^{-3/2} & N > 1 . \end{cases} \qquad (23)$$

Naturally, this is one of the possible distributions. The version involving a similar distribution $Y(N) \propto N^{-3/2} + 6N^{-6}$ has been described.[68] However, one should note that this distribution is based on experimental data up to $N \approx 90$ because $x \leqslant 90$ in the experiment and the functions $\omega_N(x)$ have a sharp maximum at $x \approx N$ for $N \gg 1$. Under such conditions, the derivation of the function $Y(N)$ for $x \gg 1$ from the decay of $L^*(x)$ at $x \gg 1$ reduces in essence to the use of the relation $Y(x) \propto L^*(x)$.

The marked difference between the forms of the relations $\omega_N(x)$ for different values of N when N and x are approximately unity justifies fairly reliable conclusions concerning the nature of the $Y(N)$ relation also when $N \approx 1$. For example, the change in the quantity $Y(1)$ by 30% from 2.5 [for the same values of $Y(N)$ with $N > 1$ as in Eqn (23) and for $\tau_{77} = 26$ min] already gives rise to a discrepancy with experiment greater than 15% in the region where $x \approx 1$ for any $Y(N)$ with $N \geqslant 1$. When account is taken of the accuracy of the determination of τ_{77} (20–35 min.) for the same values of $Y(N > 3)$ as in Eqn (23), a satisfactory agreement with experimental relations can be obtained for $Y(1) = 1.5-3.5$.

Numerical calculation has shown[64] that the theoretical form of the RTL_{bl} curve, including the maximum, agrees satisfactorily with the experimental curve for $\tau(T) = \tau_0 \exp(E/k_BT)$, where the activation energy $E = 0.65 \pm 0.05$ eV and $\tau_0 = \tau_{77} = 26$ min. An important feature is that only data on $Y(N)$ for $N \leqslant 10$, which corresponds to the range of values of x in which the RPL curve can be satisfactorily recorded, were needed to describe the initial section of the RTL_{bl} curve, including the maximum.

b. The quantum yield in the bleaching of e_{tr}^-. Isothermal decay of the optical density

The available information about the $Y(N)$ relation makes it possible to calculate the rate of change of the bleaching quantum yield or of the number of trapped electrons recombining on absorption of a single light quantum:

$$\varphi = \frac{1}{D}\frac{dD}{dx} , \qquad x = \sigma_{ph}Lt , \qquad (24)$$

where $D(t)$ is the concentration of e_{tr}^- at time t given by the following equation in the model with a single depth of traps:

$$D(t) = \sum_{N=1}^{\infty} Y(N) \sum_{i=1}^{N} \omega_i(t) . \qquad (25)$$

Numerical calculation of the $\varphi(D/D_0)$ relation from Eqns (21), (24), and (25) agrees satisfactorily with experimental data[32,97] according to the result of a number of studies.[64,68,91]

Eqns (19)–(21), (23), and (25) can be used to describe the kinetics of the isothermal decay of the optical density of e_{tr}^-. The experimental relations $\varphi(t)$ and $D(t)$ then make it possible to determine τ from the relation

$$\tau = \varphi\left(\frac{dD}{dt}\frac{1}{D}\right)^{-1} . \qquad (26)$$

The use of data[32] for φ and D in the time interval 0.3–30 h leads to $\tau = 26 \pm 3$ min.[68] The data for the isothermal decay of $D(t)$ in 3-methylpentane at 77 K, quoted in the literature,[31,32,80] are also described satisfactorily under these conditions.

Thus the approach based on the use of the distribution function for electrons with respect to the number of captures by traps before recombination makes it possible to consider from a single standpoint the kinetics of the electron–ion recombination luminescence arising both on thermo- and photo-liberation of electrons from traps in an amorphous nonpolar dielectric material.

c. Comparison of $Y(N)$ with data on the radiolysis of liquid hydrocarbons

The significance of the distribution $Y(N)$ can be readily understood by comparing data for the kinetics of the recombination of electron–ion pairs in hydrocarbon glasses with the results of the study of the radiolysis of liquid hydrocarbons. According to Rzad et al.,[106] the yield of the electron–ion pairs which avoided recombination at time t in liquid hydrocarbons is given by the relation

$$G(t) = G_0 \exp\{\lambda' t\} \operatorname{erfc}\{\lambda' t\}^{1/2} , \quad (27)$$

where $G_0 \approx 4$ is the overall initial yield of the electron–ion pairs and λ' is a constant characterising the rate of recombination. For long times ($\lambda' t \gg 1$), Eqn (27) can be expressed approximately as

$$-\frac{d}{dt}G(t) \approx \frac{\lambda' G_0}{2\sqrt{\pi}}(\lambda' t)^{-3/2} . \quad (28)$$

Eqn (28) describes satisfactorily the decay of the optical density of excess electrons in a number of liquid hydrocarbons with a relatively low mobility.[107] If it is assumed that in both liquid and solid hydrocarbons the motion of the electron can be represented as a sequence of jumps from one trap to another,[94] so that the electron spends the same time τ in each trap, then one can write the following expression for the electron–ion recombination in a liquid:

$$G(t) = G_{tr}^0[1 - \zeta(t)] , \quad (29)$$

where $\zeta(t)$ is the probability of the neutralisation of the pair at time t. Since we have

$$d\zeta_N = \frac{1}{\tau}\omega_N(t)\,dt , \quad (30)$$

for pairs executing N transitions between traps before recombination, we obtain from Eqns (21), (29), and (30)

$$\frac{d\zeta}{dt} = \sum_{N=1}^{\infty} Y'(N)\frac{d\zeta_N}{dt} = \frac{1}{\tau}\sum_{N=1}^{\infty} Y'(N)\omega_N\frac{t}{\tau} , \quad (31)$$

where

$$Y'(N) = \frac{Y(N)}{\sum_{N=1}^{\infty} Y(N)}$$

is a function normalised with respect to unity. We have from Eqns (29) and (31)

$$-\frac{dG(t)}{dt} = G_{tr}^0\frac{1}{\tau}\frac{\sum_{N=1}^{\infty} Y(N)\omega_N\frac{t}{\tau}}{\sum_{N=1}^{\infty} Y(N)} . \quad (32)$$

For $N \gg 1$, the functions $\omega_N(t)$ have a single sharp maximum at $t_{max} \approx N\tau$. Therefore we obtain from Eqns (28) and (32) for $t \gg \tau$ and $t \gg (\lambda')^{-1}$

$$\frac{\lambda' G_0}{2\sqrt{\pi}}(\lambda' t)^{-3/2} \approx G_{tr}^0\frac{1}{\tau}\frac{Y(t/\tau)}{\sum_{N=1}^{\infty} Y(N)} . \quad (33)$$

It follows from Eqn (33) that $Y(N) \approx N^{-3/2}$ for $N \gg 1$. This result agrees with Eqn (23) obtained for solid hydrocarbons. In other words, for the same spatial distribution of thermalised electrons and positive ions in the liquid and solid phases, the photostimulated recombination time for an electron executing N jumps is proportional to the number of these jumps: $t_r \propto N$.

IV. Electric polarisation of electron–ion pairs

The conductimetric method, involving the recording of changes in the electric conductivity of the specimen on exposure to a short ionising radiation pulse, is the most direct procedure for the investigation of the kinetics and mechanisms of chemical reactions of charged species in a condensed phase. If only free ions participate in conduction, the conditions governing the application of this method are evident. However, such a relatively simple situation arises in nonpolar substances when most of the generated charges, having an initial inhomogeneous distribution in space, have already reacted. The contribution to the electric conduction by 'bound' charges (for example, the electrons of geminate pairs recombining in the absence of acceptors over short periods) requires special consideration.

1. Characteristic features of the relaxation of the electrical conductivity induced by ionising radiation in low-molecular-mass hydrocarbons

Polarisation by an external electric field may result in the participation of electron–ion pairs in nonstationary electrical conduction. The kinetics of the polarisation current of such pairs differ significantly from the kinetics of the polarisation current for the usual mechanisms of the polarisation of dielectric substances associated with the inhomogeneity of the specimens, the nonuniformity of the generation of current carriers, etc. Indeed the recombination of the electron with its 'own' positive ion implies zero integral charge transfer:

$$\int_0^{\infty} I_r dt = 0 , \quad (34)$$

which should lead to an unusual involvement of this electron in conduction. The unusual feature consists in the fact that, for example, in a constant electric field, the electron initially contributes to the conduction and then 'takes back' this contribution, moving against the external electric field.

This feature of the electrical conduction by electrons participating in pair recombination was apparently first noted by Frankevich and coworkers.[108,109] Later, similar considerations were used in the interpretation of the results of the study of quasi-stationary electrical conductivity,[10,11,110–112] thermostimulated current,[60,70] and photoconductivity[10,59,68,112–116] induced by ionising radiation in an organic dielectric substance.

For a sufficiently high intensity of light with a wavelength in the region corresponding to the absorption by e_{tr}^-, a decrease in the photocurrent as a function of time is observed after an initial increase. This can be explained by the decrease in the concentration of the trapped electrons.[10,113]

For isooctane at 77 K, the decrease in photoconductivity is described by a hyperbolic relation.[68] For 3-methylpentane and methylcyclohexane, the form of the initial section of the curve describing the decrease in photoconductivity $\bar{\omega}_{ph}(t)$ is independent of the dose up to 10^5 rad,[68] while the rate of decrease corresponding to longer times rises with increase in dose.[59] The form of the photocurrent decrement curves for $x = \sigma_{ph}Lt < 30$ in 3-methylpentane ($L \approx 10^{14}$ photons cm^{-2} s^{-1}) remained unchanged, within the limits of experimental error, for a tenfold alteration in the γ-irradiation dose, whereas for $x > 30$ the form of the curves depended significantly on the dose.

Direct measurements of the polarisation current of electron–ion pairs in the 3-methylpentane glass at 77 K have been undertaken.[113] An increase in the electrical conductivity (radiation conductivity) of solid 3-methylpentane at 77 K was observed directly on exposure to γ-radiation. The time required to establish a quasi-stationary value of the current I_γ was shorter than the time taken to measure the current, whilst I_γ was independent of the duration of γ-irradiation up to doses of ~0.1 Mrad.

The characteristic time variations of the photocurrent induced by IR light in a solid dielectric material (for example, in 3-methylpentane) for different combinations of the electric potential on the electrodes during (V_γ) and after (V_{ph}) exposure to radiation are presented in Fig. 3.

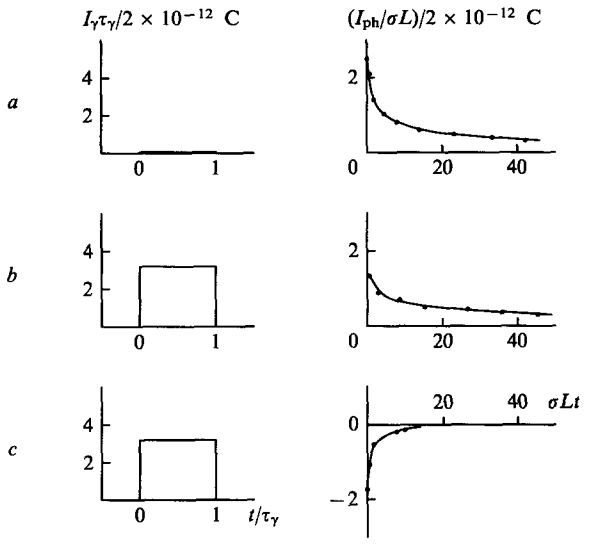


Figure 3. Time variation of the current due to the γ-induced conductivity and of the photocurrent for different combinations of the potential on the electrodes of a 3-methylpentane specimen at 77 K during γ-irradiation and IR illumination.[113] Dose 0.01 Mrad, λ = 1600 nm, $L = 3 \times 10^{14}$ photons cm^{-2}: (*a*) $V_\gamma = 0$, V_{ph} = 1 kV; (*b*) V_γ = 1 kV, V_{ph} = 1 kV; (*c*) V_γ = 1 kV, $V_{ph} = 0$.

In the case where $V_\gamma = 0$ and V_{ph} = 1 kV, the $I_{ph}(x)$ relation (Fig. 3*a*) is similar to that obtained by Yakovlev and coworkers.[59,68] Fig. 3 shows that the application of an electric field (V_γ = 1 kV, V_{ph} = 1 kV) during γ-irradiation (Fig. 3*b*) is accompanied by a decrease in the initial value and in the rate of decrease in the photocurrent (λ = 1600 nm) compared with the $I_{ph}(x)$ relation for the first case. For V_γ = 1 kV and $V_{ph} = 0$ (Fig. 3*c*), a reverse photocurrent or depolarisation current, comparable in absolute magnitude with the photocurrent in the case illustrated in Fig. 3*a*, is observed. Comparison of the normalised current amplitudes $\tilde{I}_\gamma = I_\gamma\tau_\gamma$ and $\tilde{I}_{ph} = I_{ph}/L$ shows that $\tilde{I}_\gamma : \tilde{I}^a_{ph} : \tilde{I}^b_{ph} : \tilde{I}^c_{ph} = 1 : 0.7 : 0.4 : 0.5$. Under these conditions, $\int_0^{\tau_\gamma} \tilde{I}_\gamma dt = \int_0^\infty \tilde{I}_\gamma dt$ with an accuracy to within 50%.

2. Kinetics of conduction in the presence of transcapture

a. Dependence of the current kinetics on the number of electron capture steps

If the photoconductivity is due to the involvement of free electrons, in the absence of recombination (which corresponds to the linear section of the $I_{ph} \propto D_r$ relation) the decrease in photoconductivity as a function of illumination time at the wavelength corresponding to the e^-_{tr} absorption band can be represented as follows:[68]

$$\tilde{\omega} = \frac{\tilde{\omega}_0}{1 + k_r\tau_0 n_0 L\sigma_{ph} t}, \tag{35}$$

where $\tilde{\omega}_0 = en_0\mu_0\tau_0 L\sigma_{ph}$, $n_0 = GD_r$ is the initial concentration of free electrons, and k_r, μ_0 and τ_0 are respectively the recombination reaction rate constant, the mobility, and the lifetime of an electron liberated by light from a trap to the conducting state.

Since the photoconductivity decrement curves in isooctane are described satisfactorily by Eqn (35), the present authors assume[68] that the free charges are responsible for the main component of the photocurrent, i.e. $I_{ph} \approx I_{fi}$. Furthermore, the ratio $k_r/\mu_0 \approx 10^{-6}$ cm V, calculated using Eqn (35) and the measured quantity $(d\tilde{\omega}/dt)|_{t=0}$, proved to be $\sim 4\pi e/\varepsilon$, which is characteristic of free charges for the Langevin recombination law. The $\tilde{\omega}(t, D_r)$ relation for 3-methylpentane is not described by Eqn (35); the quantity k_r/μ_0, calculated formally using Eqn (35), proved to be much greater than $4\pi e/\varepsilon$, which indicates that the photocurrent in 3-methylpentane is associated with charges recombining in pairs,[68] i.e. $I_{ph} \approx I_{gi}$.

The difference between the kinetics of the photocurrent in isooctane and 3-methylpentane can be understood if one takes into account the difference between the values of $\mu_0\tau_0$ for these substances. The product $\mu_0\tau_0$ determines the number of steps N in which an electron is captured during its motion towards the positive ion. For an isolated pair of charges (e^-_{tr} and a positive ion), we have

$$N \approx \frac{t_r}{\tau_0}, \tag{36}$$

where $t_r \approx r_0^3\varepsilon/3e\mu_0$ is the recombination time for a pair with an initial distance r_0 without allowance for the lifetime in the localised state. For $N \approx 0$ and a constant duration of the recording of the current $\tau_d \gg \tau_0$, there is no photocurrent due to bound charges. The occurrence of even one transcapture of an electron by a trap and hence a contribution by the bound pair of charges to the photoconductivity should be expected when

$$\mu_0\tau_0 < \frac{r_c^3}{3e} \approx 5 \times 10^{-9} \text{ cm}^2\text{V}^{-1}. \tag{37}$$

For isooctane, $\mu_0\tau_0 \gg 10^{-8}$ cm^2V^{-1} and, on the photoabstraction of an electron from a trap, the bound charges recombine without repeated capture. On the other hand, for 3-methylpentane $\mu_0\tau_0 \ll 10^{-9}$ cm^2V^{-1} and, in the case where $r_0 \approx r_c$ and $G \approx 0.1$, the number $N \sim 10^3$.

By postulating the involvement of only free electrons in conduction, it is difficult to explain the independence of the form of the photocurrent decrement curve of the irradiation dose observed for $x < 30$[59] and the linear dependence of the amplitude of the reverse current I^c_{ph} on the γ-irradiation dose D_γ. On this hypothesis, the appearance of the reverse current could be attributed to the formation of a space charge in the regions near the electrodes, but in this case one would have to expect that $I^c_{ph} \propto D^2_\gamma$.

On the other hand, the form of the $I_{ph}(x)$ and $I_{ph}(D_\gamma)$ relations, the ratios of the amplitudes of the photocurrents in the cases presented in Fig. 3 and of the radiation conductivity current can be described satisfactorily if it is assumed that the observed current is determined largely by the polarisation of the electron pairs.[113]

Taking into account the differences between the characteristics of the changes in the induced electrical conductivity in different hydrocarbons, it is frequently possible to divide the photocurrent induced by the ionising radiation into two components:[10,68]

$$I_{ph} = I_{gi} + I_{fi}, \tag{38}$$

where I_{fi} and I_{gi} are the parts due to the free and bound electrons respectively.

b. Polarisation of electron–ion pairs

Numerous studies have been devoted to the analysis of the behaviour of an isolated pair of ions initially located in a dielectric medium at short distances from one another. The use of the Onsager model[15] is apparently most justified for thermalised pairs in a nonpolar liquid.[2] The influence of an external electric field on the behaviour of the pair has been considered in a number of investigations,[17,117,118] but the effect of the external field on the electric dipole moment of the pair has been little investigated within the framework of this model.

If the pairs are isolated and only thermalised electrons‡ in a conducting state, with a constant mobility μ_0 ($\approx 1\ cm^2\ V^{-1}\ s^{-1}$ for 3-methylpentane at 77 K [119]) and having an initial spherically symmetrical distribution with respect to radii, participate in the polarisation, then the radiation and photoconductivity currents can be expressed in the form [113]

$$I_\gamma = \frac{1}{\tau_\gamma}\sum_{N=1}^{\infty} Y(N) q_0^N \ , \tag{39}$$

$$I_{ph} = \sum_{N=1}^{\infty} Y(N) I_q^N(t) \ . \tag{40}$$

Under these conditions, we have for the photocurrent $I_q^N(t)$, determined by electrons executing N jumps before recombination,

$$I_q^N(t) = \sum_{i=1}^{N} q_i^N \omega_i(t) \frac{1}{\tau} \ , \quad \frac{1}{\tau} = \sigma L \ , \tag{41}$$

where q_i^N is the charge, averaged for pairs with different initial orientations, transferred to an external circuit either during the period from the instant of the generation of the electron to its capture by the trap (q_0) or during the time taken for the transfer of the electron from the ith to the $(i+1)$th localised state($q_{i\neq 0}$).

According to the present authors, [68, 113] the hypothesis that the dependence of the distance r between the positive ion and an electron on the residence time of the electron in the conducting state t_0 is determined mainly by the drift of the ion in the electric field is justified for the estimation of q_i in weak external electric fields. The average number of captures of an electron with an initial distance r_0 from the positive ion before recombination is defined by Eqn (36). This leads to a value of q_0^N approximately equal to the charge transferred along the direction of the external field by the free electron during its lifetime before capture by the trap: [68, 70]

$$q_0^N \approx q_0 = \frac{e\mu_0\tau_0 E}{d} \ , \tag{42}$$

where d is the distance between the electrons.

The model considered describes satisfactorily the characteristics of the variation of the radiation conductivity current in a nonpolar dielectric substance [111] and the ratio of the currents for different combinations of the electric potential on the electrodes of the specimen during exposure to ionising radiation and photoexcitation of e_{tr}^-. [59, 68, 113]

If the pairs interact with one another, then, in view of the possibility of the recombination of the electron with a foreign ion, one cannot generally speaking neglect the contribution to the conductivity by electrons recombining after preliminary capture by a trap and Eqn (34) cannot be regarded as valid, as in the case of isolated pairs. However, in view of the fact that the Coulombic field (generated by all the charges at the location of the given electron), averaged with respect to all the electrons at the site of their thermalisation, is zero ($E_k' = 0$), Eqn (42) remains in force for the polarisation current also in the case of interacting pairs. [68, 113]

3. The diffusion-drift model

In the early investigations, [68, 113, 120] the polarisation of the pairs was considered without taking into account the diffusion of the species. This approximate approach did not allow, in principle, the study of significant features such as the appearance of a negative current and the change in the current at long times. The kinetics of the electric polarisation of an isolated pair of ions have been studied [112, 116, 121–123] on the hypothesis that the ions execute Brownian motion in the Coulombic field of their partners and in the weak external electric field (see also the review of Tyutnev et al. [11]).

If the current of free electrons I_{fi} is adopted as the unit current and the mobility is assumed equal to the overall mobility of the positive and negative ions, then the polarisation current of N isolated pairs can be expressed in the form [112]

$$I(t) = \frac{1}{e\mu NE}\frac{d}{dt}P_E(t) \ , \tag{43}$$

where P_E is the projection of the overall electric moment of all the pairs on to the direction of the electric field $\boldsymbol{E}$ generated by the charges at the electrodes. In view of the axial symmetry of the problem, we have

$$P_E(t) = N\int_0^\infty \int_{-1}^{1} 2\pi e r^3 n(r, \tilde{\mu}, t)\, d\mu\, dr \ , \tag{44}$$

where r is the distance between the ions of the pair, $n(r, \tilde{\mu}, t)$ is the density of the probability of finding a pair of ions with the parameters r and $\tilde{\mu}$, and $\tilde{\mu} = \cos\theta$.

We shall assume that the charged species execute Brownian motion in the Coulombic field of their partners $\boldsymbol{E}_c$ and in the external field $\boldsymbol{E}$ and recombine when they approach an oppositely charged species to a distance a approximately equal to the molecular size. The calculation of the current then reduces to the solution of the Smŏjuchowski equation

$$\begin{cases} \dfrac{\partial n}{\partial t} = -\operatorname{div} \boldsymbol{J} \\ \boldsymbol{J} = -D\vec{\nabla} n + \mu(\boldsymbol{E}_c + \boldsymbol{E})n \end{cases} \tag{45}$$

with the initial and boundary conditions

$$n(r, \tilde{\mu}, 0) = f(r) \ , \tag{46}$$

$$n(a, \tilde{\mu}, t) = 0 \ , \tag{47}$$

where D is the overall diffusion coefficient of the positive and negative ions. The case where it is possible to neglect the diffusion of the species and to consider only their drift in the electric field is simplest to analyse. Since the ratio of the rates of diffusion and drift diminishes with decrease in temperature, this case corresponds to low temperatures.

a. Low temperatures

If one neglects the diffusion of the species, the problem reduces to finding the time variation of the radius vector $\boldsymbol{r}(r_0, \tilde{\mu}, t)$ for a pair of ions the relative positions of which are described by the equation

$$\frac{d\boldsymbol{r}}{dt} = \mu(\boldsymbol{E}_c + \boldsymbol{E}) \ . \tag{48}$$

The significance of the notation is clear from Fig. 1.

The polarisation current has been examined [112] for four types of spherically symmetrical initial distributions, usually postulated in order to interpret the kinetics of ionic processes in photochemistry and radiation chemistry: [124, 125] the δ-function and the exponential Gaussian, and displaced Gaussian $\{f(r) \propto \exp[-16(r-b')^2/(b')^2]\}$ distributions (b' is a constant). For the $f(r) \propto \delta(r - r_0)$ distribution and short times, the polarisation current is approximately equal to the current of the same number of free ions; with increase in t, the current initially increases and then, following the onset of recombination, falls and becomes negative.

It is not difficult to understand such variation of the current. Taking into account Eqns (43) and (48), we have

$$I \propto \bar{E} = \bar{E}_c + E \ , \tag{49}$$

‡Only those electrons which during their lifetime before recombination t_r have been captured by a trap at least once are of interest; the electrons recombining without being captured by a trap do not contribute to the measured current in view of Eqn (34) and the relation $t_r \approx \tau_0 \ll \tau_d$.

where $\bar{E}$ and $\bar{E}_c$ are respectively the projections of the $E_c + E$ field averaged for all the pairs and of the field E_c on to the direction of the external field. $\bar{E}_c \approx 0$ for $t \approx 0$, so that the initially $I \propto E$, as for free ions. As a result of the motion of the ions, the pairs for which the vectors E_c and E are pointed in the same direction fall within the regions of a stronger Coulombic field sooner than the pairs with the opposite orientation. This leads to an increase in $\bar{E}$ and hence to an increase in I. The monotonic increase in the current occurs before the onset of recombination. The pairs for which the directions of the fields E_c and E are identical are the first to begin recombining. The dipole moment of such a pair is $p < 0$, so that the onset of their destruction leads to an abrupt increase in the current. A similar variation of the current (from negative values to zero) occurs when recombination is completed. The maximum absolute negative and positive currents are approximately equal to $5aE_c^0/r_0E$, where $E_c^0 = e/\varepsilon r_0^2$.

In contrast to the distribution $f(r) \propto \delta(r - r_0)$, in the case of other distributions the current initially diminishes monotonically with increase in t, becomes negative, and then increases, tending to zero. For sufficiently wide distributions ($b' \gg a$), the maximum negative current is almost independent of b'. Under these conditions, the values of I_{max}^-/I_{fi} for these distributions are respectively 6×10^{-3}, 0.09, and 0.6.[112]

b. Allowance for the diffusion of ions

Various approaches have been used for the numerical solution of Eqn (45).[17,117,118] The most rigorous and general method of solution, proposed by Noolandi and Hong,[117,118] is based on the calculation of the Green's function for Eqn (45). Since solutions for smooth initial distribution $f(r)$ are usually of interest, in analysing the experimental data it is more convenient to use a simpler approach to the numerical solution of Eqn (45)—the method of finite differences. The difficulties which arise in the solution of Smołuchowski's equation, subject to the boundary condition (47), by this method were associated with the high gradient $n(r, \tilde{\mu}, t)$ at the boundary, which requires the application of small steps. However, we may note that, for the attraction potential between the ions and $a \leqslant 1$ nm, the rate of destruction of the species near the boundary is mainly determined not by diffusion but by the drift of the species in the Coulombic field. Therefore in many cases the numerical calculation can be significantly simplified[112] by dividing the region corresponding to the solution into two parts: the narrow boundary region in which it is possible to neglect diffusion, i.e. one can put $D = 0$ in Eqn (45), and the main region where Eqn (45) is solved without neglecting the diffusion of the species subject to the following condition at the inner boundary:

$$\left.\frac{\partial n}{\partial r}\right|_{r=a'} = 0 \ . \qquad (50)$$

Fig. 4 presents the results of the calculation of the pair polarisation current for the initial exponential and displaced Gaussian distribution functions.[112] The same figure also illustrates the time variation of the 'survival' function $\Omega(t)$ for the overall number of pairs of ions at time t. For $t \geqslant 0.2r_c^2/D$, the values of $\Omega(t)$ obtained correspond to the asymptotic formula[17]

$$\Omega(t) = \Omega_\infty\left(1 + \sqrt{\frac{r_c^2}{\pi Dt}}\right) .$$

The time variation of the average field $\bar{E} = I(t)/\Omega(t)$ has a minimum at $tD/r_c^2 \approx 10^{-4} - 10^{-3}$, which is associated with the polarisation of the spatial distribution of the geminal electrons in the external field.[123]

The characteristic features of the polarisation current arising after the formation of ion pairs at $t = 0$ in a permanent electric field can be summarised as follows:

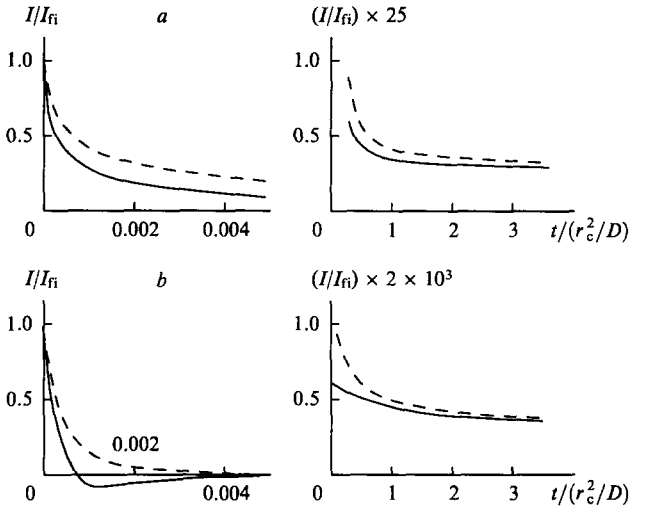


Figure 4. Time variation of the current calculated from the numerical solution of the Smołuchowski equation for the exponential initial distribution (*a*) and a displaced Gaussian distribution (*b*) of the pairs.[112] $a = 0.05r_c$, $b' = 0.1r_c$; the time variation of the probability of the survival of the pairs $\Omega(t)$ is shown dashed.

1. For the exponential and Gaussian distribution functions of the pairs with respect to the initial distances between the ions, the polarisation current is initially [for $\Omega(t)/\Omega(0) \geqslant 0.5$] approximately equal to the current due to the same number of free ions.

2. The maximum negative current I_{max}^- depends significantly on the form of the initial distribution.

3. Allowance for the diffusion of the species (or transition to high temperatures) leads to the appearance, at long times, of a direct current associated with the separation of ion pairs into free charges (Fig. 4). The maximum negative current I_{fi} diminishes with increase in temperature and the time when the current changes sign increases. Whether or not this current is negative depends on the form of the distribution.

c. Induced photoconductivity in the 'two states of the electron model'

The kinetics of the current due to the geminate ions have been frequently discussed by many investigators.[68,112–116] However, all these studies were concerned solely with thermalised charged species. On the other hand, the observed influence of the wavelength of the IR illumination on the yield of free charges (see below) shows that the characteristic features of the stage involving the thermalisation of the electrons liberated from traps by light are important for the description of the kinetics of the processes with their participation.

In order to take this factor into account, a model has been proposed[53,126,127] postulating that the photoexcitation of e_{tr}^- creates nonthermalised 'hot' electrons e_{hot}^-, which undergo a transition to a new trapped state having passed through the stage involving the thermalised state e_0^-. This hypothesis does not conflict with the idea that the electron is trapped in a molecular medium, which was put forward by Mozumder.[128] Furthermore, if one assumes that the drift displacement Δ_{hot} of e_{hot}^- in a single electric field is negligibly small § compared with the displacement Δ of a thermalised electron e_0^- during the period before its solvation, i.e. $\Delta_{hot} \ll \Delta$, then an additional term must be included in the Smołuchowski equation in such a 'two-step' model for the description of the diffusion and drift of charged species.

§ The hypothesis is based on the estimate $\Delta_{hot} = 4 \times 10^{-13}$ cm^2 V^{-1} for hydrocarbon liquids similar to 3-methylpentane with a low mobility of the excess electrons[129] and on the estimate $\Delta \approx 5 \times 10^{-12}$ cm^2 V^{-1} for the photoliberated electron in the 3-methylpentane glass at 77 K.[126]

The calculation of the photocurrent $I(t)$ can be reduced to the calculation of a new distribution function $f_i(r,\theta)$ for the pairs $\{e_{tr}^-, M^+\}$ after the ith e_{tr}^- photoionisation step:

$$I(t) = \frac{1}{d}\frac{dP_E}{dt}, \tag{51}$$

where P_E is the projection of all dipoles on to the direction of **E**:

$$P_E(t) = \sum_{i=0}^{N} p_i \omega_i(\sigma_{ph} L t), \tag{52}$$

$$p_i = eN \int 2\pi r_i^2 \sin\theta \cos\theta f_i(r,\theta)\, d\theta\, dr. \tag{53}$$

Here p_i is the projection of the dipole moment of the pairs for which the trapped electrons have been photoionised i times onto the direction of E and $\omega_i(x) = x_i \exp(-x)/(i!)$ is the Poisson function. The function $f_i(r,\theta)$ is given by

$$f_i(r,\theta) = \int n(r,\theta,t)\,\tau_0^{-1}\, dt, \tag{54}$$

where τ_0^{-1} is the rate constant for the reaction $e_0^- \rightarrow e_{tr}^-$, and $n(r,\theta,t)$ is the density of e_0^- defined by the Smołuchowski's equation

$$\frac{\partial n}{\partial t} = -D_0 \Delta n + \mu_0 (E_c + E)\,\mathrm{grad}\, n - \tau_0^{-1} n, \tag{55}$$

subject to the initial condition

$$n(r,\theta,t=0) = n_i(r,\theta) = \int b(|r - r'|) f_{i-1}(r,\theta)\, d(r')^3. \tag{56}$$

Here E_c is the Coulombic field, $b(a)$ is the distribution of e_{hot}^- with respect to the thermalisation lengths, and $D_0 = \mu_0 k_B T/e$ and μ_0 are respectively the average diffusion coefficient and the mobility of e_0^-. Thus in this model $\Delta = \mu_0 \tau_0$. If the form of the distributions $b(a)$ and $f_0(r,\theta)$ is known, then in this approach one can estimate $I(t)$ from the experimental values of $\mu_0\tau_0$ and σ_{ph}.

It has been shown [53] that the two states model predicts a marked dependence of the photocurrent, induced by the excitation of the geminate electrons, on the thermalisation length for the liberated electron. In this case, the spectral dependence of the photocurrent, normalised with respect to the optical absorption of e_{tr}^-, may depend on the wavelength of the exciting light even when the ionisation quantum yield is unity throughout the absorption band of e_{tr}^-. Therefore the conclusion concerning the nature of the optical absorption of e_{tr}^-, postulating that it is due to the transition to a bound state and based on the difference between the photocurrent and optical absorption spectra for geminate electrons, as well as the use of the equations of the usual homogeneous kinetics for the photocurrent cannot be regarded as sufficiently justified.

V. Thermo- and photo-stimulated separation of electron–ion pairs

Despite the fact that a large number of publications have been devoted to the localisation of excess electrons in nonordered molecular media, the mechanism of this process remains unelucidated. [128,130–137] Three cases have been differentiated in the formation of thermodynamically stable localised electrons: thermalisation, localisation, and solvation:

$$e_{hot}^- \rightarrow e_{qf}^- \rightarrow e_{loc}^- \rightarrow e_{sol}^-. \tag{57}$$

These describe the degradation of the energy of the 'hot' electrons e_{hot}^- with formation of a quasi-free electron e_{qf}^- and the solvation of the electron e_{loc}^- localised beforehand (for nonpolar media — the 'trapped' electron e_{tr}^-). By virtue of the effective application of the optical absorption method, most data have been accumulated on e_{tr}^-. However, very little is known about the precursors of e_{tr}^- and, in particular, about the spatial evolution of the low-energy electrons during their transformation into e_{sol}^- or e_{tr}^-. On the other hand, this process involves the migration of e_{hot}^- before thermalisation, the migration of the thermalised electron e_{qf}^- before thermalisation, and also the possible displacement of e_{loc}^- during solvation.

In discussing the processes involving the thermalisation of low-energy electrons in hydrocarbon glasses, three stages are also differentiated: [138,139] (1) excitation of the electronic states of molecules with a threshold energy of ~6 eV; (2) intramolecular excitations for electron energies in the range $6 \geqslant E_e \geqslant 0.4$ eV; (3) excitation of the rotational and intermolecular vibrations for $E_e < 0.4$ eV. For solid amorphous dielectric substances, the available information about the spatial distributions of thermalised $[F(r)]$ and trapped $[F_{tr}(r)]$ electrons is extremely limited and is based mainly on the analysis of the few existing data concerning the radiation yield of free ions.

1. The influence of the external electric field on the radiation yield of free ions

The method based on the integration of the thermostimulated current, arising on heating specimens γ-irradiated at low doses at 77 K, has been applied [67,70] to the determination of G_{fi} in 3-methylpentane and methylcyclohexane. The integral Q of the difference between the currents I_{TCT} for γ-irradiated and non-irradiated specimens in 3-methylpentane is proportional to the irradiation dose D_γ for $D_\gamma < 10$ rad. A similar $Q(D_\gamma)$ relation for methylcyclohexane has been obtained in the dose range <3 rad. The quantity Q and the linear relation $Q(D_\gamma)$ indicated that most of the charged species generated by the ionising radiation in the space between the electrodes were drawn on to the electrodes and did not recombine in the bulk of the specimen. [140] The radiation yield of the separated pairs of charges in 3-methylpentane has been estimated from the linear section of the $Q(D_\gamma)$ relation. [67,70]

$$G_{fi}(E = 6 \times 10^3 \text{ V cm}^{-1}) = \frac{Q}{\rho v D_\gamma} = 1.2 \times 10^{-2} \text{ (1 pair per 100 eV)}, \tag{58}$$

where v is the volume between the electrodes.

In order to determine G_{fi} in a zero field, a method similar to the cleaning field method [22] applied to liquid dielectric substances has been used. [70] According to the results of a study of thermostimulated recombination luminescence of γ-irradiated 3-methylpentane, on heating 3-methylpentane above 77 K the electron–ion recombination is largely complete at ~90 K. Therefore, if after γ-irradiation of 3-methylpentane the specimen is initially heated at $E = 0$ to ~90 K and then recooled and again heated at $E \neq 0$, then most of the electron–ion pairs will be separated in a zero field. The number of electron–ion pairs separated on heating in a zero field has been determined [70] by integrating I_{TCT} on reheating the specimen in the field $E_{TCT} = 6 \times 10^3$ V cm^{-1}. $G_{fi}(0) = (6 \pm 1) \times 10^{-3}$ pairs of free ions per 100 eV of the absorbed radiation energy has been obtained for the 3-methylpentane glass. The observed value of $G_{fi}(0)$, like that of G_{fi} for $E_\gamma = E_{TCT} \neq 0$, was referred to the temperature 85 ± 5 K.

The same method has been applied [70] to the determination of $G_{fi}(0)$ in methylcyclohexane with the sole difference that the specimen γ-irradiated at 77 K was subjected to preliminary heating to ~100 K. This temperature corresponds to the region in which the methylcyclohexane RTL peak is observed. [141,142] The yield of the separated pairs of charges in methylcyclohexane is $(2.0 \pm 0.03) \times 10^{-2}$ per 100 eV; it was referred to the temperature $T \approx 100 \pm 10$ K at which most of the electron-ion pairs are separated. [70] As was to be expected from Eqn (1), in the low field limit the $G_{fi}(E)$ relations in 3-methylpentane and methylcyclohexane were found to be linear.

2. The influence of IR illumination on G_{fi}, the rate of recombination, and trapping

It has been observed [143] that the IR illumination of a γ-irradiated 3-methylpentane specimen before heating increased I_{TCT} appreciably. Since the optical absorption in the range 600–2000 nm of 3-methylpentane γ-irradiated at 77 K is mainly due to the trapped electrons, the increase in G_{fi} on IR illumination was attributed [143] to the fact that electron–ion pairs are separated more effectively on photoliberation of e^-_{tr} than during the thermoactivated motion of the charged species.

According to Onsager, [15] the probability of the separation of charged species (within the framework of diffusion-drift ideas concerning the separation of ion pairs in thermal equilibrium with the medium) is independent of their diffusion coefficients and is defined by Eqn (3). Assuming that Eqn (3) is valid for the electron–ion pairs in γ-irradiated 3-methylpentane, the increase in G_{fi} on IR illumination has been attributed [70, 143] to the formation of hot electrons [having an average kinetic energy greater than $\frac{3}{2}k_BT$] on IR illumination. This hypothesis agrees with the interpretation of the optical absorption of e^-_{tr} in 3-methylpentane in the range 600–2000 nm as being due to the direct transition to a continuum, [30, 40, 132] since a photoliberated electron e^-_{hot} is then formed in the initial stage of reaction (8):

$$e^-_{tr} + h\nu \rightarrow e^-_{hot} \quad . \tag{59}$$

It has an initial kinetic energy $E_0 = h\nu - E_t$, where $h\nu$ is the energy of the light quantum and $E_t = 0.5$ eV [38, 40] is the threshold energy of the photoabstraction of e^-_{tr}.

a. Dependence of G_{fi} on the energy of the bleaching light quantum

It has been observed [70, 143] that, on IR illumination, G_{fi} increases with the duration of bleaching and with increase in $h\nu$ (Fig. 5), reaching the limiting values $G^{h\nu}_{fi}$. This can be understood if the estimated distance $l \approx 80$ Å which the mobile electron e^-_m traverses in 3-methylpentane at 77 K before localisation [144] is adopted and if account is taken of the fact that the distance from the positive ion to most of the e^-_{tr} ($\sim 10^2$ Å) [25] is much smaller than $r_c \approx 10^3$ Å, i.e. the electron must execute several transitions from one localised state to another before it escapes from its positive ion. The number of such transitions can be estimated from the relation

$$N \approx \frac{r_c^2}{l^2} \approx 200 \ .$$

As for the separation of pairs in the dark, the $G^{h\nu}_{fi}$ relations proved to be linear.

Analysis showed [70] that the increase in the yields $G^{h\nu}_{fi}$ limiting in terms of the bleaching time, with decrease in the wavelength of the bleaching light cannot be related to the distribution of traps with respect to the electron photoabstraction threshold E_t: if after bleaching by light with a wavelength of 2000 or 1800 nm the specimen is also bleached by light with $\lambda = 1000$ nm, the effect is smaller than for light with $\lambda = 1000$ nm alone (Fig. 5).

The observed increase in G_{fi} following the additional bleaching of the specimen by light with $\lambda \approx 1000$ nm [70, 143] can be associated with the fact that, after prolonged bleaching by light (for example with $\lambda \approx 2000$ or 1800 nm), a proportion α of the total number of e^-_{tr} before the start of bleaching still remains in the vicinity of their 'own' positive ions. An estimate [70] yielded the following values of α: 0.18 ($\lambda \approx 2000$ nm) and 0.13 ($\lambda \approx 1800$ nm). Hence it follows that the structural traps with a photoabstraction threshold $E_t > 0.65$ eV constitute only a small proportion $\delta \approx 10^{-3}$ in 3-methylpentane.

b. Participation of hot electrons in reactions

The influence of IR illumination on the yield of free electrons and also on the recombination luminescence [84–86] caused by free electrons confirms the participation of hot electrons in photostimulated electron–ion recombination processes. It may be expected that the hot electron is appreciably involved also in other reactions initiated by the photoionisation of the trapped electron. This is apparently indicated by data [44, 145–147] which permit the hypothesis that the effectiveness of the trapping of an electron by an alkyl radical [44] and certain halogen-containing acceptors [147] in solid hydrocarbons is different in the photo- and thermostimulated liberation of electrons from traps.

The involvement of hot electrons in the formation reaction of pyrene dimers in 3-methylpentane at 77 K has been demonstrated. [85, 86] An increase by a factor greater than 20 in the intensity of the RTL peaks associated with the dimer luminescence of pyrene, arising as a result of the reaction of free ions on photobleaching of e^-_{tr}, was observed in these investigations.

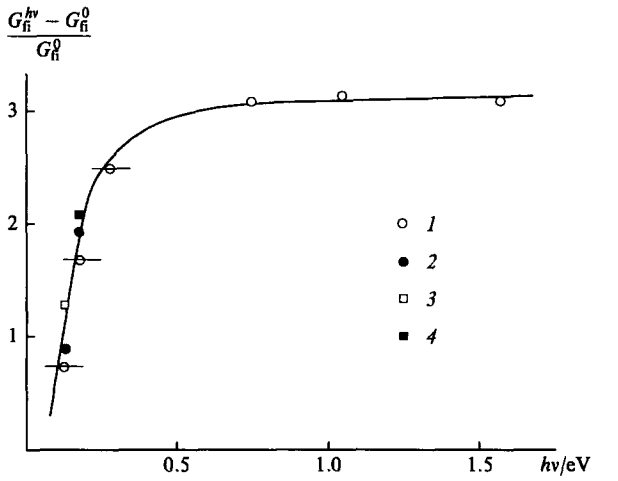


Figure 5. Dependence of the yield of free ions in 3-methylpentane on the energy of the bleaching light quantum: [70] (*1*) bleaching by light at a single wavelength; (*2*) allowance for ions remaining after bleaching; (*3*) point obtained after illuminating the specimen initially by light with $h\nu = 0.62$ eV and then by light with $h\nu = 1.2$ eV; (*4*) point obtained after illumination initially by light with $h\nu = 0.69$ eV and then by light with $h\nu = 1.2$ eV.

3. Drift displacement of the photoliberated electron in a unit electric field

Measurements of the radiation conductivity and the induced photoconductivity have proved hitherto the most reliable method for securing data on the drift displacement of electrons in a unit field $\mu_0\tau_0$. These data are usually quoted as the product $G\mu_0\tau_0$, where G is understood as the radiation yield of the charges participating in the conduction and μ_0 and τ_0 are the mobility and the lifetime in the conducting state. According to Ametov et al., [113] the dependence of the specific radiation electrical conductance on the power of the radiation J for γ-irradiated 3-methylpentane can be expressed as $\tilde{\omega} = 10^{-19} J\,\Omega^{-1}\,\mathrm{cm}^{-1}\,\mathrm{rad}^{-1}\,\mathrm{s}$. For the electronic mechanism of the radiation conduction in solid saturated hydrocarbons, this relation yields the product [10]

$$G\mu_0\tau_0 = \frac{10^2\tilde{\omega}}{eJ} = 1 \times 10^{-12}\ \mathrm{cm^2\,V^{-1}}. \tag{60}$$

In order to determine $G\mu_0\tau_0$ on UV- and γ-excitation, many workers [10, 30, 40, 50, 51, 54, 148] investigated the induced photoconductivity in hydrocarbons. The initial slope of the dependence of the conductivity on the dose $\tilde{\omega}(D_r)$ makes it possible to estimate the quantity

$$G\mu_0\tau_0 = \frac{1}{e\sigma_{ph}L}\frac{d\tilde{\omega}}{dD_r} \ . \tag{61}$$

This quantity is different in crystalline and amorphous hydrocarbons. For example, for isooctane, methylcyclohexane, and 3-methylpentane which have been specially freed from electron

acceptors, its values are[68] 1.2×10^{-7}, 2.3×10^{-10}, and 0.8×10^{-12} $cm^2 V^{-1} eV^{-1}$ respectively (the radiation yield G was calculated per 100 eV of the energy absorbed in 1 cm^3). The value of $G\mu_0\tau_0$ obtained in 3-methylpentane at 77 K agrees to within 30% with the estimate[113] based on measurements of the radiation conductivity. When account was taken of the quantities G and β', the photoconductivity data led to a drift displacement of the electron in 3-methylpentane at 77 K $\mu_0\tau_0 = 1.6 \times 10^{-12}$ $cm^2 V^{-1}$,[68] which is close to the value 1.5×10^{-12} $cm^2 V^{-1}$.[51]

Nevertheless one should note (despite such agreement between the experimental data of different workers) that the majority of the estimates were made under the conditions of the photoexcitation of the electrons of geminate pairs.[126] The estimation of $\mu_0\tau_0$ requires in this case a detailed analysis of the contributions of the free and bound charges to the photoconductivity, which is not a simple task.[53,112]

Apparently there has been only one study[59] in which the photocurrent in γ-irradiated 3-methylpentane at 77 K was measured over sufficiently long times such that almost complete separation of the pairs $\{e_{tr}^-, M^+\}$ occurred. Together with the yield of free ions, $G_{fi}^{h\nu} = 0.05$, measured during the photobleaching of a γ-irradiated specimen under the same conditions ($h\nu = 1.2$ eV and $E = 6 \times 10^3$ V cm^{-1}), and the photoionisation quantum yield $\beta' \approx 1$,[70] these data lead to $\mu_0\tau_0 = (5 \pm 1) \times 10^{-12}$ $cm^2 V^{-1}$.[59,126]

4. Spatial distribution of thermalised and trapped electrons

The G_{fi} data for solid dielectric materials make it possible to obtain information about the initial spatial distribution of the thermalised electrons $F(r)$ using Eqn (4), as for liquid systems. Furthermore, the yields G_{fi} obtained make it possible to infer the initial spatial distribution of trapped electrons $F_{tr}(r)$ from the radiation yields of such electrons G_{tr}^0:

$$G_{fi}(0) = G_{tr}^0 \int_0^\infty F_{tr}(r) \exp\left(-\frac{r_c}{r}\right) dr \ , \tag{62}$$

where $F_{tr}(r)$ is a function normalised with respect to unity.

The numerical calculation of $G_{fi}(0)$ by Eqn (4) using simple distributions $F(r)$ [functions (5)–(7)] has been carried out.[70] For $G_0 = 4$,[23,149] agreement of both function (5) and (7) with experimental yields $G_{fi}(0)$ was obtained (with $b \approx 60$ Å for 3-methylpentane and $b = 70$ Å for methylcyclohexane). The values of b found are close to the analogous quantities known for the same hydrocarbons in the liquid phase. Such a result might have been expected on the hypothesis of approximately the same electron thermalisation processes in liquid and solid amorphous hydrocarbons. However, if an exponential distribution [Eqn (5)] is postulated also for $F_{tr}(r)$, then Eqn (62) with $G_{tr}^0 = 0.8$ for 3-methylpentane[32] and $G_{tr}(0) = 6 \times 10^{-3}$ yields $b = 105$ Å,[70] which is significantly greater than the analogous distribution parameter for thermalised electrons. When the characteristic features of the electron thermalisation process are taken into account within the framework of the two states model (see Section VI), other results are obtained.

If the increase in G_{fi} on IR illumination is attributed to the fact that the kinetic energy of the electron e_m^- is higher than the thermal energy, then it is natural to assign to such an electron an effective temperature T_{ef}. T_{ef} may be estimated from the quantity $G_{fi}^{h\nu}(0)$ in a zero field from a relation similar to Eqn (62):

$$G_{fi}^{h\nu}(0) = G_{tr}^0 \int_0^\infty F_{tr}(r) \exp\left(\frac{-e^2}{\varepsilon k_B T_{ef} r}\right) dr \ . \tag{63}$$

Calculation of the dependence of T_{ef} on the energy of the bleaching light quantum[70] by means of Eqn (63) from G_{fi} data,[143] based on the hypothesis that the function $F_{tr}(r)$ is exponential with the parameters $b = 105$ Å and $G_{tr}^0 = 0.8$,[32] shows that, for $h\nu < 0.6$ eV, the temperature T_{ef} differs little from the temperature of the medium. But, after an increase in $h\nu$, the temperature T_{ef} initially rises rapidly and then, for $1.0 < h\nu < 2.5$ eV, hardly changes and amounts to ~140 K. A satisfactory agreement between the calculated and experimental temperatures T_{ef} for $h\nu < 0.8$ eV was achieved with $E_t = 0.5 \pm 0.1$ eV. The small change in T_{ef} with increase in $h\nu$, for $h\nu > 0.1$ eV, may be associated with the postulated[138] sharp increase in the rate of consumption of the electron energy on excitation of intramolecular vibrations in the region of the kinetic energy of the electron ~0.4 eV.[150]

The use of the Onsager formula might be justified by the fact that the photoliberated electron is captured many times (~200) by traps before it escapes from the 'Coulombic well' of its ion. Indeed, within the framework of the Onsager model, ϕ is independent of the mechanism of the migration of species. In essence, the probability of the separation of the pair is determined by the competition between two processes: the diffusional motion of the species during the transition between localised states, leading on average to the 'escape' of the species from the centre, and its displacement to the centre as a result of the drift in the Coulombic field of the ion during the same period. The first process may be characterised by the mean square of the distance between the successive localised states (l_s^2) and the second by the mean displacement Δ between the localised states in a unit field. For a thermalised species, the ratio of these quantities,

$$\frac{l_s^2}{\Delta} = 6\frac{k_B T}{e} \ , \tag{64}$$

corresponds to the Einstein relation

$$\frac{D}{\mu} = \frac{k_B T}{e} \ ,$$

because the diffusion coefficient $D = l_s^2/6\tau$ and the drift mobility $\mu = \Delta/\tau$, where τ is the time of the transition between localised states.

However, the participation of nonthermalised species in the migration process would seem to infringe Eqn (64). In order to avoid this contradiction, it has been suggested[53,126,127,151] that the effective temperature be defined by the relation

$$T_{ef} = \frac{e}{6k_B}\frac{l_s^2}{\Delta} \ . \tag{65}$$

This approach makes it possible to determine the ratio l_s^2/Δ from the values of $G_{fi}^{h\nu}$ obtained after prolonged bleaching of the irradiated specimens and to find l_s^2 from the known value of Δ. Estimation of the lower limit yields $l_s \approx 20$ Å[151] on the basis of the results of Yakovlev et al.[70]

A more detailed approach to the description of the separation process, based on the application of the two states model, has been used.[126] The following estimates were made: the mean square thermalisation distance in 3-methylpentane $l_{hot} \approx 49$ Å, the mean square distance traversed by the thermalised precursor of the electron $l_0 \approx 45$ Å, the mean square solvation distance $l_s = (l_{hot}^2 + l_0^2)^{1/2} \approx 66$ Å, and the effective temperature $T_{ef} \approx 169$ K. The following feature may be noted: if it is assumed that the estimates[144,152] refer not to l_{hot} (as claimed by the authors) but to l_s, then the values of l_s quoted by Yakovlev[126] agree also with the estimated values of ~80 Å for 3-methylpentane (injection of electrons at 77 K)[144] and of ~65 Å for methylcyclohexane (thermoluminescence).[152]

The mean square electron thermalisation length in 3-methylpentane estimated by Yakovlev[126] agrees also with the experimental data for the thermalisation of low-energy electrons (20–60 Å) in liquid hydrocarbons with a low electron mobility. Various methods were used to obtain these data: photoemission from metals into a liquid,[153] electron transport across thin films,[154] and photoionisation of liquid solutions.[155–159]

The above value is also close to the analogous value for liquid solutions,[160,161] although its monotonic increase with increase in the energy of the electrons, observed in a later study,[162] is outside the calculated limits of the error[126] in the range of electron energies 0.5–2 eV.

If it is assumed that the electrons generated by the ionising radiation are localised like the photoliberated electrons, then, in order to determine $f_0(r)$ by Eqns (54) and (55), it is necessary to have data only on the initial distribution of the thermalised electron–ion pairs and the product $\mu_0\tau_0$. Best agreement with experimental results has been achieved[53] using in the calculation the distribution of the trapped electrons $f_0(r)$ corresponding to the initial distribution of the thermalised pairs and consisting of two parts: a Gaussian function with a maximum of 20 Å and a half-width of 35 Å and an exponential function which begins at 240 Å with a parameter of 70 Å (the overall density of the second part is ~5% under these conditions). Similar distributions of pairs with respect to thermalisation lengths and with a high initial density and a long 'tail' had been postulated also in previous studies in order to interpret data on the yield of free ions in liquid hydrocarbons[19,163] and for the description of the kinetics of recombination luminescence in glasses.[83]

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