Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

# Yield of Carrier Generation in Organic Solids Under Electron Bombardment. II

M. Schott [a]

[a] Groupe de Physique des Solides de l'Ecole Normale Supérieure Tour, 23 9 quai Saint-Bernard, Paris, 5e

Version of record first published: 28 Mar 2007.

To cite this article: M. Schott (1970): Yield of Carrier Generation in Organic Solids Under Electron Bombardment. II, Molecular Crystals and Liquid Crystals, 10:4, 399-409

To link to this article: http://dx.doi.org/10.1080/15421407008083501

*Molecular Crystals and Liquid Crystals.* 1970. Vol. 10, pp. 399–409

Printed in Great Britain

# Yield of Carrier Generation in Organic Solids Under Electron Bombardment. II

M. SCHOTT

Groupe de Physique des Solides de l'Ecole Normale Supérieure†
Tour 23
9 quai Saint-Bernard
Paris 5e

*Received February* 10, 1970

**Abstract**—The yield of carriers generated in organic solids by electron bombardment, or by X- or $\gamma$-rays, should be independent of the primary electron energy above 5 keV, independent of the field applied to the solid between $\sim 10^3$ and a critical field of about $10^4$ V/cm at room temperature, and roughly proportional to temperature in this range. Above the critical field, the observed yield should increase with the applied field and be very weakly temperature dependent. The comparison of the yields in different materials is a way of investigating the mechanisms of thermalization of secondary electrons, as the only other material-dependent parameter, the optical dielectric constant, is only slightly variable.

The yield of carriers generated by low energy (MeV) protons, deutons and alpha-particles should be proportional to the particle track length, and should vary with temperature and with electric field (normal to the track), approximately as the yield under electron bombardment.

## 1. Introduction—The Model Used

In this note, we discuss some implications of a model recently proposed(1) to account for the results obtained by Delany and Hirsch in their study of electron-bombarded anthracene(2): a yield of one pair for 400–450 eV, independent of the energy of the primary electron, and of the field applied to the anthracene crystal to collect the charges, at least up to $10^4$ V/cm. Another explanation had been put forward(3): that most of the generated electrons recombine with their "parent" hole ("initial recombination", first discussed by Onsager(3)); this is a monomolecular process. We shall compare its implications with those of the present model, in Sec. 3.

---

† Laboratoire associé au C.N.R.S.

The *model used* is basically the following: most of the pairs created do separate, that is, " initial recombination " of pairs is unimportant, and does not account for the low yield found. But the carriers thermalize essentially inside the cylindrical track, or roughly spherical spur, where they were created. In these small volumes, the carrier density is initially very high. The carriers can leave these volumes by diffusion, if the field applied to the solid is low, or by drift in that field if it is high enough. On the other hand they can recombine *bimolecularly* inside the spur, or track. The order of magnitude of the number of carriers left for collection will then be essentially determined by the extent of bimolecular recombination before diffusion or drift begins to be effective: for short times, the correct approximation is the reverse of that assumed by Jaffé(4) in his theory of columnar recombination (prescribed diffusion). In the previous paper(1) only the low field case was considered.

One can obtain easily an upper limit of the critical field, above which drift takes over diffusion in competing with recombination, by comparing in the differential equation for the time variation of the carrier density

$$\frac{\partial n}{\partial t} = \mu\mathscr{E} \operatorname{grad} n + \mathscr{D}\Delta n - \mathscr{R}np$$

the first, drift, term to the second, diffusion, term, at $t = 0$, as Kramers first noticed.(5) The ratio of these two quantities is $\approx kT/e\mathscr{E}R_0$ where $R_0$ is the radius of the track, or spur. Using—for anthracene for instance—$R_0 \approx 150$ Å we get $\mathscr{E}_{\text{crit}} \approx 2\ 10^4$ V/cm at 300 °K. Fields lower, resp. higher than this critical field, will be referred to below as low, resp. high, fields. Around the critical field, diffusion, drift, and electrostatic interaction of the charge clouds will all be comparable.

## 2. Field and Temperature Dependence of the Quantum Yield Limited by Columnar Recombination

### 1. LOW APPLIED FIELDS

Assuming for simplicity an isotropic solid, the characteristic time for relaxation by diffusion is $\sim R_0^2/4\mathscr{D}$ and the number of carriers escaping recombination from a cylindrical track of length $\lambda$ is(1):

$$N_c \approx \frac{4\pi \mathscr{D}}{\mathscr{R}} \lambda \tag{1a}$$

and for a spherical spur of radius $R_0$

$$N_s \approx \frac{4}{3} \frac{4\pi \mathscr{D}}{\mathscr{R}} R_0 \tag{1b}$$

where $\mathscr{D}$ is the diffusion coefficient and $\mathscr{R}$ the recombination rate constant of the carriers. The applied field does not, of course, appear, and in this range, the yields are predicted to be *independent of the applied field* $\mathscr{E}$, if the recombination of a carrier with a carrier of opposite sign from another spur is negligible, that is, for not too low fields.

As an electron forms a cylindrical track in the last 2500–3000 Å of its range only, all its energy in excess of ~3 keV is deposited in spurs, and the number of collected carriers is predicted to be *proportional* to the number of spurs, that is *to the primary energy.*(1) A secondary electron of high initial energy will similarly lose energy by forming at first spurs, and then a track. The number of tracks therefore increases with the primary energy, but the total energy deposited in tracks is always a small fraction of the primary energy as soon as the latter is about 10 keV.(6) In addition, diffusion is less effective in tracks than in spurs, so that the number of collected charges is determined by $N_s$, times the number of spurs, and not by $N_c$.

In the case of low-energy heavier particles (protons, deutons, α-particles) the ionization loss is much larger, and a cylindrical continuous region of excitation is generated along the track. Formula (1a) will apply simply, provided the energy of the incident particle is low enough, so that no high-energy secondary electron is generated. The carrier yield is then *proportional to the track length*, not to the incident particle energy (non constant yield).

In both cases, Eq. (1) give an upper limit: as the electron and hole clouds expand together, recombination will continue, lowering a little more the number of collected charges. Comparing the numerical predictions of Eq. (1b) with the experimental results for anthracene,(2) one expects a further decrease by a factor of 2.

Both formulae contain only $\mathscr{D}/\mathscr{R}$. But $\mathscr{D} = (kT/e)\mu$ and it was shown long ago by Langevin(7) that in dense gases $\mathscr{R} = (\mu_+ + \mu_-)e/\epsilon\epsilon_0$, and we know that this applies also in aromatic crystals provided $\mu/\epsilon$ is replaced by a suitable space average.(8) Therefore, we can rewrite (1)

$$N_c \simeq \frac{2\pi \epsilon\epsilon_0 kT\lambda}{e^2} \tag{2a}$$

and

$$N_s \simeq \frac{8\pi}{3}\frac{\epsilon\epsilon_0 kTR_0}{e^2} \tag{2b}$$

The extra factor of $\frac{1}{2}$ coming from $\mu_+ \approx \mu_-$.

The energy loss mechanisms of particles and electrons are not expected to be much temperature dependent, and therefore the yields will be approximately *proportional to* $T$, provided the field is large enough to make carrier trapping and space charge effects negligible, so that columnar recombination is the only carrier loss mechanism. Preliminary results seem to confirm this dependence.(9)

The yields depend on the material only through $\epsilon$, $\lambda$ and $R_0$. Equations (2) then allow some simple predictions. For instance, all aromatic hydrocarbons have $C/H$ ratio between 1 and 2, and the loss under particle bombardment are mainly due to carbon, therefore they will all have comparable yields, proportional to their dielectric constant, and to the inverse of their density. The dielectric constant to be considered in polar materials depends on the frequency of their relaxation processes. As all columnar recombination is over in a few $10^{-11}s$, generally the optical, and not the static, dielectric constant should be chosen. They may however be exceptions, such as $C(CH_3)_3Cl$ whose relaxation lies at millimeter wavelengths. Through $R_0$, the yield under electron bombardment will be sensitive to the thermalization processes, and this gives a simple method for investigating these processes.

## 2. High Applied Fields

Large fields can be sustained by good quality aromatic crystals (above $10^5$ V/cm) and even larger fields by plastic sheets (up to $10^6$ V/cm). Let us therefore consider their influence in a simple model, applicable to electron excitation: we approximate a spur by a spherical volume (radius $R_0$) filled at time $t = 0$ with uniform and equal densities $n_0$ of electrons and holes, that is, we assume the thermalization of electrons having a few eV's kinetic energy to be infinitely rapid. This is a serious limitation, as in a time $10^{-11}s \sim R^2/4\mathscr{D}$ a carrier with $\mu \approx 10^2$ cm²/Vs drifts by 100 Å in a field of $10^5$ V/cm. The analysis is therefore valid only for materials in which the thermalization processes are very rapid, as seems to be in aromatic hydrocarbons.

Let $\mathscr{E}$ be the applied field, $\mu^* = \mu_+ + \mu_-$ in the direction of $\mathscr{E}$. Neglecting diffusion and electrostatic interaction of the clouds, the total number $N_s'$ of pairs left when the electrons and holes clouds are separated is

$$N_s' = \int_0^\infty n(t)\, dV_r(t) \tag{3}$$

where $n(t) = n_0\ (1 + \mathscr{R} n_0 t)^{-1}$ is the recombination-limited density and $V_r(t)$ the volume of clouds overlap. Then

$$N_s' = N_0\,[\tfrac{3}{2}(\xi - \xi^3)\log(1 + \xi^{-1}) + \tfrac{3}{l}\xi^2 - \tfrac{3}{4}\xi]$$

if $\xi = \mu^* \mathscr{E}/2R_0 \mathscr{R} n_0$. The high field limit $\xi \ll 1$, which has probably no physical meaning, gives

$$N_0' \approx N_0\left[1 - \frac{9\mathscr{R}}{16\pi R_0^2\,\mu^* \mathscr{E}} N_0\right]$$

Conversely, if $\xi \ll 1$, that is $\mathscr{E} < (3N_0/2\pi R_0^2)(\mathscr{R}/\mu^*) \sim 5.10^5$ V/cm in anthracene

$$N_s' \approx \frac{\pi R_0^2 \mu^*}{\mathscr{R}}\,\mathscr{E}\,[K - \log \mathscr{E}] \tag{5}$$

with $K = \log[(3N_0/2\pi R_0^2)(\mathscr{R}/\mu^*)] - \frac{1}{2}$. Here again, $\mathscr{R}$ and $\mu^*$ enter only through $\mathscr{R}/\mu^* = e(\epsilon\epsilon_0)^{-1}$ if Langevin theory applies. A large increase of the carrier mean free path and therefore of $\mu^*$, or a large change in the mobility anisotropy could cause a deviation from the above value of $\mathscr{R}/\mu^*$ at large fields, but we know that neither happens at least up to $2.10^5$ V/cm at 300 °K in anthracene.(10)

In this range $\mathscr{R}/\mu^*$ will be about the same, and independent of temperature, in all non-polar organic solids, and the properties of thermal carriers do not play any role in the observed yield.

At high fields, say a few $10^4$ V/cm, we expect the yield of carriers under electron bombardment to be approximately *independent of temperature and proportional to the applied field and the primary electron energy.* It can vary for different materials due to difference in the thermalization processes, expressed in $R_0^2$. $N_0$ entering only through its log in (5), it will be difficult to get information about the initial yield in this range also.

However, at still higher fields, and at least above

$$\mathscr{E} \approx \frac{3N_0 e}{2\pi R_0^2 \epsilon\epsilon_0}$$

$N \to N_0$ and the initial yield may be obtained. These were the conditions where Martin and Hirsch$^{(11)}$ recently obtained yields of about 1 pair per 30 eV at very high fields ( ~10 V/cm) in thin plastic sheets.

The case of a heavier particle, forming a cylindrical track, is similar. The effect of the electric field component perpendicular to the track will also be to separate two cylindrical charge distributions. The problem has been considered by Kramers$^{(5)}$ for slightly different conditions. As for electron bombardment, one finds at very high fields

$$N_c = N_0\left(1 - \frac{K_c N_0}{\mathscr{E} \sin \alpha}\right)$$

and at lower fields:

$$N_c = K_s \lambda \mathscr{E} \sin \alpha [K_s' - \log (\mathscr{E} \sin \alpha)]$$

$\alpha$ being the angle between the axis of the column and the direction of $\mathscr{E}$, assumed to be different of zero. $K_c$, $K_s$ and $K_s'$ depend somewhat on the exact initial carrier distribution assumed (uniform, gaussian etc.). The same qualitative conclusions as for electron bombardment are therefore valid for particles; the yield will be less variable for different materials, as only $R_0\lambda$, and not $R_0^2$ enters in $N_c$, and will depend on the angle $\alpha$. All these conclusions are summarized in Fig. 1, for the case of electron bombardment.

## 3. Field and Temperature Dependence of the Quantum Yield with Initial Recombination

In the theory of initial recombination, a similar expression is obtained.$^{(3)}$ If the electron is thermalized at a distance $r$ from its parent hole, then the escape probability is at zero field exp—$r/r_c$ where $r_c$ is a critical distance

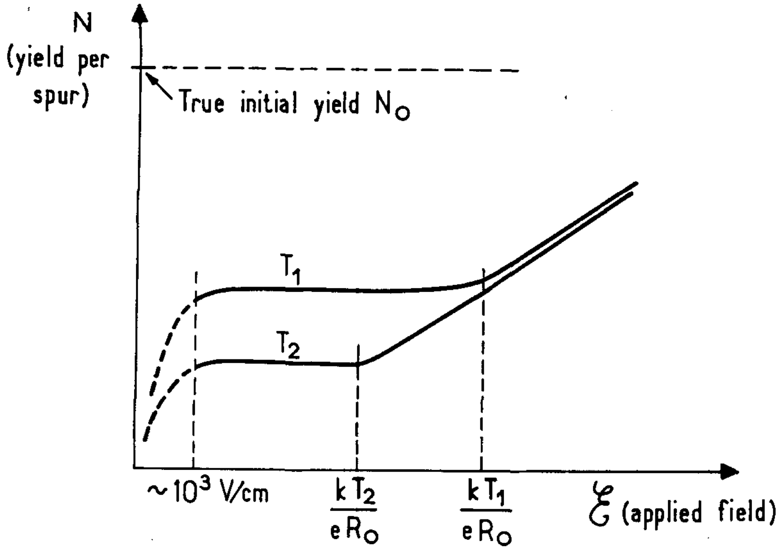

Figure 1. Yield *vs* electric field curve for electron bombardment. $N$ is proportional to the primary energy throughout. In the low field region $N \alpha T$. At high fields (not shown) the yield will saturate and reach the value $N_0$. In anthracene, the critical field $kT/eR_0$ is about $2.10^4$ V/cm at 300°K, assuming $R_0 \sim 150$ Å.

$$r_c = \frac{e^2}{4\pi\epsilon\epsilon_0 kT} \tag{6}$$

The mean escape probability $P$ has been computed by Schmidt and Allen⁽¹²⁾ assuming that the thermalization distances have a gaussian distribution of mean $b$, which may or may not depend on the electron initial kinetic energy.

$$P = 4\pi^{-1/2}\int_0^\infty x^2 \exp\left[-x^2 - \frac{r_c}{bx}\right] dx \tag{7}$$

For anthracene, we know from secondary emission and from Perkins' experiments⁽¹⁵⁾ that initially one pair is created per 27–30 eV deposited in the crystal. But only one pair per $\gtrsim$ 400 eV is collected for clearing fields $\lesssim 10^4$ V/cm, hence $P \lesssim 0.07$ corresponding to $b/r_c \lesssim 0.3$ hence $b \lesssim 70$ Å in contradiction with the value obtained in the secondary emission experiments: 70 Å to decay only to a final kinetic energy $\gtrsim 1.6$ eV (electron affinity of the anthracene crystal).

Let us compare the predictions of the " initial recombination " theory as regards the temperature dependence. When $b/r_c$ varies from 0.35 to 0.1, $P \alpha (b/r_c)^{2.8}$ to a very good approximation. Below 0.1, $P$ decreases even more rapidly. Hence, should initial recombination be dominant, the observed quantum yield, extrapolated to zero field, would be close to $\alpha T^{2.8}$ between 100 and 300 °K if we assume $b$ constant. Such a temperature dependence is actually found in saturated hydrocarbon liquids between 270 and 370 °K.(12)

Therefore a precise measurement of a temperature dependence of the quantum yield under electron bombardment will be of considerable help in choosing between columnar and initial recombination. It has also been shown by Onsager(3b) that the field dependence of the quantum yield, when limited by initial recombination is of the form

$$\eta = \eta_0 \left(1 + \frac{e^3}{2\mathscr{D}k^2T^2}\mathscr{E}\right) \tag{8}$$

that is, the yield should increase linearly with the field, extrapolate at zero field to a finite value, which however is unobservable due to other competing processes (trapping, general bulk recombination...). Experimental results published up to now(2) do not agree with this, showing a constant yield, when corrected for trapping, up to $10^4$ V/cm. However, when an anthracene crystal is excited with UV photons just above the gap, generating very low energy electrons ($<1$ eV kinetic energy), the field dependence of the quantum yield follows a law similar to (8), with $r_c \sim 100$ Å, indicating that initial recombination is dominant for these very low energy hole-electron pairs.(13)

However, $e^3/2\mathscr{D}k^2T^2$ is a small quantity, and the necessary corrections make the yield-field curve somewhat uncertain, so that these results cannot reliably enough distinguish between columnar and initial recombination under electron bombardment.

## 4. Delayed Recombination Luminescence

Finally, we may mention yet another possible crucial experiment: in a given pair, created from a singlet ground state molecule, the electron and hole spin are correlated. If initial recombination takes place before this correlation is lost, only singlet excited states will be formed in recombination, a small fraction of which—2% at 300 °K—will decay through the triplet state by intersystem crossing. Very few triplets will be formed by recombination in this case, and delayed fluorescence will be very faint. In columnar recombination, as the electron and the hole come, generally, from different pairs, there will be no such correlation, and by columnar recombination singlets and triplets will be formed in the same ratio as in ordinary bulk recombination, that is 3 triplets per singlet.(14) In fact, as we already noted, columnar recombination is just one form of bulk recombination. In this case, recombination will generate a very intense delayed fluorescence. In electron excitation, as a relatively small number of pairs is generated within a given spur, there might be some residual spin correlation, that is, a given electron has a non-zero probability to recombine *by chance* with its parent hole, and a triplet-to-singlet ratio slightly smaller than 3 will not contradict the columnar recombination hypothesis.

In his experiments, using electrons generated by X-ray irradiation on anthracene crystal, Perkins(15) finds a total triplet-to-singlet ratio of 1.5; but some singlets, and a smaller number of triplets, are generated by the electrons, and the final ratio for excitons generated by recombination is probably close to 3.

This result is in agreement with the columnar recombination hypothesis. It can be reconciled with initial recombination if the spin correlation is lost in a time much shorter than the time needed for the excited electron of the pair to thermalize. It is generally agreed that this latter time is very short, $10^{-13}$ to at most $10^{-12}s$. Only a very efficient process can be invoked to reverse the electron spin so rapidly. We shall not treat this problem quantitatively here. However, we should note that intersystem crossing rate constants in the singlet manifold are much smaller than needed here. Also the rate constant at threshold (kinetic energy of the electron, 1.8 eV), for the exchange process by which the electron loses energy and a triplet exciton is created, as calculated by Hernandez(16) and without any allowance for vibrational overlap which would decrease it, is only $10^{9}s^{-1}$, which falls short by 4 orders of magnitude. Possible flaws in Hernandez's theoretical treatment, such as neglect of configuration interaction of discrete states with a continuum, would hardly account for this discrepancy, and the spin randomization during thermalization will probably not occur.

Even if the randomization does occur, the initial recombination will account for Perkins' results only with an additional *ad-hoc* assumption: as each spin reversal generates one triplet, a very large triplet-to-singlet ratio is now possible, and one must assume that just enough electrons generate triplets, to give a final ratio equal to that observed in bulk recombination. This assumption can be contradicted only by looking at materials other than anthracene, as such a compensation is not likely to occur very often.

## 5. Conclusion

Therefore, in addition to the field dependence already mentioned,(1) the temperature dependence of the quantum yield, and the importance of delayed fluorescence generated by carrier recombination, give two other ways of testing the relative importance of columnar and initial recombination. In the case of an aromatic hydrocarbon crystal, such as anthracene, irradiated with electrons—directly or through X-rays—the experimental results up to now favor the columnar recombination.

Initial recombination in anthracene should be a relatively inefficient process, dominating only when the electron is generated with a small kinetic energy.

## Acknowledgements

This work was supported by the D.G.R.S.T. under contracts 66.0299.01 and 70.02.159.

### REFERENCES

1. Schott, M., *Mol. Cryst.* **5**, 229 (1969), Paper I.
2. Delany, J. and Hirsch, J., *J. Chem. Phys.* **48**, 4717 (1968).
3a. Kepler, R. G. and Coppage, F. N., *Phys. Rev.* **137**, 610 (1966).
3b. Onsager, L., *Phys. Rev.* **54**, 554 (1938).
4. Jaffe, G., *Ann. Phys.* (4) **42**, 303 (1913).
5. Kramers, H. A., *Physica* **18**, 665 (1952).
6. Hummel, A. and Allen, A. O., *J. Chem. Phys.* **46**, 1602 (1968).

7. Langevin, P., *Ann. Chim. et Phys.* **28**, 287, 433 (1903).
8. Morris, R. and Silver, M., *J. Chem. Phys.* **50**, 2969 (1969).
9. Sansal, B., Private communication.
10. Hoesterey, D. C., unpublished.
11. Martin, E. H. and Hirsch, J. *Sol. St. Comm.* **7**, 783 (1969). However in this paper $\mathscr{R}$ and $\mu$ seem to be mutually inconsistent.
12. Schmidt, W. F. and Allen, A. O., *J. Phys. Chem.* **72**, 3730 (1968).
13. Hornig, J. F., Batt, R. H. and Braun, C. L., Abstracts, 4th Molecular Crystal Symposium P. 126 (1968).
14. Helfrich, W. and Schneider, W. G., *J. Chem. Phys.* **44**, 2902 (1966).
15. Perkins, W. G., *J. Chem. Phys.* **48**, 931 (1968).
16. Hernandez, J., *Phys. Rev.* **169**, 746 (1968).