BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 595—599 (1971)

Inter and Intramolecular Charge and Excitation Transfer Observed in Irradiated Polyvinyl Chloride Particles with Surface-coated Additives

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(Received May 27, 1970)

Particles of polyvinyl chloride were coated with small amounts of various aromatic compounds from benzene solutions and were then irradiated in a vaccum. The ESR spectra of the specimen thus obtained were recorded. Though the amount of the coated additives, in the ratio of 1 molecule for 100 monomer units of PVC, was small, strong effects on the ESR spectra were observed. The additives coated on the surface affect the ESR spectra in two ways. They cause a decrease in the total ESR absorption intensity; this was observed with all the additives studied. They also often transform the ESR spectrum; this was observed with several additive compounds, such as *p*-benzoquinone, tetramethylphenylenediamine-2·HCl, chrysene, hydroquinone, nitrosonaphthol, perylene, and diphenylpicrylhydrazine. Only the conduction of the excitations, holes and electrons formed in the bulk particles, to the surface of the particle can explain these results. On the surface of the particle, the excitation or the electric charge is transferred to the additive by means of an intermolecular interaction with it. The possibilities for the mechanism of the conduction of the excitation and the electric charges, and the ionization processes are discussed.

Ueda and his co-workers studied the ESR spectra of γ-irradiated polyvinyl chloride (to be abbreviated as PVC) and their trans-formations in the presence of various gases.[1-5] Some of the anomalies observed in these transformations were ascribed to free radical transformations. In the past decade, much evidence for ionic processes has been found for the systems including alkyl halide-aromatic hydrocarbon solutions in both the solid and liquid phases.[6-10] It seems quite obvious, however, that free radical interpretations do not wholly account for the observed phenomena.[5] Therefore, it is necessary to reinvestigate the ESR of irradiated PVC from a different point of view.

The results of the kinetic studies of the pulse radiolysis of the alkyl halide-aromatic hydrocarbon solutions showed that only the "conduction theory" of the ions and possibly their precursors explains the kinetic data obtained. Therefore, it seems desirable to test further the possibilities of the conduction of the radiation-induced activated species across a particle of PVC.

The transient species generated in radiation-chemical systems are observed either by a quick-detection method or by trapping them in some stable forms. Many experiments have been done by trapping them in frozen rigid glass.[9,10] It has also been possible to trap them on porous solid surfaces. For this reason, we expected to find some stable ionic species on the surface of PVC which are trapped and stabilized at room temperature.

Experimental

The PVC powder used in this study was Vinychlon 4000L of the Mitsui Toatsu Chemical Co.; it contained no additives. The particle were all below 50 mesh in size. 0.500 g of PVC (8 mmol of $-CH_2CHCl-$ equivalent) and 0.08 mmol of additive were mixed, and then 2.0 m*l*, or more if needed, of benzene was poured onto it in order to dissolve the additive completely. The mixture thus prepared was kept in the air at room temperature under a dust cover to evaporate the solvent. The sample thus obtained, *i. e.*, the PVC particles coated with an additive, was placed in a spectrosil ESR sample tube; the tube was evacuated to 10^{-4} mmHg and then sealed off. Irradiation was made with 1.5 kCi ^{60}Co source to the dose of 6.65×10^4 rad (referred as D_1) and 7.315×10^5 rad (referred as D_2) at 20°C.

In this work, the number of unpaired electrons trapped in the specimen must be determined, together with their physical states. For this reason, the quantitative measurements were carried out as follows. A microwave output of 9V54 was attenuated to exactly 1/10, thus maintaining the same incident powder. The crystal current of the detector, 1N23C, was always adjusted to the same value, 0.08 mA, by adjusting the dielectric rod in one of the arms of the magic

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tee. 100 kHz phase-sensitive amplifier was allowed to stand for at least three hours prior to use. The overall signal intensity was checked and calibrated by using standard specimens, such as dispersed charcoal in alumina powder sealed in a vacuum, and Mn^{2+} ions diluted with MgO.

Results

The intensities of the ESR absorption for D_1 are listed in Table 1. The paramagnetic species, which is observed in the PVC without any additive and which shows the ESR spectrum of Fig. 1a when irradiated to D_1 in a vacuum, is written as S·. The S· has been described as a free radical in the early literature,[1,2] but its true nature has not been known exactly. Its observed amount is written as r_0. The amount of S· obtained with the PVC with an additive at the same dose is written as r. The r/r_0 ratio is shown in Table 1. The amount of the species which is obtained at the dose of D_1, and which shows the ESR spectra shown in Figs. 1b and 1c, is written as r_+. The r_+/r_0 ratio is also shown in Table 1. The same values for D_2 are listed in Table 2. In Table 2, the spin concentration (divided by r_0) due to the species, which was unaffected by bleaching the sample in air, A^+-left, is also shown. In Figs. 1—3, the ESR spectra obtained from the PVC-perylene, PVC-hydroquinone, PVC-*p*-benzoquinone, PVC-α-nitroso-β-naphthol, and PVC-β-nitroso-α-naphthol specimens are shown. Figure 1b′ indicates that there are eight almost equivalent protons which interact with the unpaired electron. Figure 1c indicates that at the dose of D_2, the spectrum resembles Fig. 1a more than Fig. 1b (see Tables 1 and 2) with respect to r_+/r_0. The same tendencies may be found in Fig. 2. In Fig. 3b, the hyperfine splitting is better resolved than in Fig. 3a because the absorption due to S· had been bleached by

TABLE 1. THE CONCENTRATIONS OF VARIOUS SPECIES AFTER IRRADIATION TO D_1

Additive	r/r_0	r_+/r_0	$1-r/r_0$	$1-r_+/r_0$ $-r/r_0$
p-Benzoquinone	0.000	0.793	1.000	0.207
Tetramethylphenylenediamine -2·HCl	0.000	0.377	1.000	0.622
Chrysene	0.000	0.179	1.000	0.821
Fluorene	0.008	0.092	0.992	0.901
2,3-Benzophenanthrene	0.106	0.008	0.894	0.887
3-Methylcholanthrene	0.113	0.000	0.887	0.887
Dibenzoanthracene	0.191	0.153	0.809	0.656
Hydroquinone	0.202	0.462	0.798	0.336
α-Nitroso-β-naphthol	0.216	0.195	0.784	0.588
trans-Stilbene	0.271	0.000	0.729	0.729
o-Terphenyl	0.281	0.000	0.719	0.719
Anthracene	0.292	0.000	0.708	0.708
β-Nitroso-α-naphthol	0.304	0.127	0.696	0.569
Styrene	0.306	0.000	0.694	0.694
Triphenylbenzene	0.318	0.034	0.682	0.648
Perylene	0.324	0.173	0.676	0.503
Phenanthrene	0.333	0.000	0.667	0.667
Pyrene	0.333	0.000	0.667	0.667
m-Terphenyl	0.370	0.000	0.630	0.630
Triphenylethylene	0.380	0.000	0.620	0.620
Naphthalene	0.385	0.000	0.615	0.615
p-Terphenyl	0.401	0.000	0.599	0.599
Diphenylpicrylhydrazine	0.406	0.497	0.594	0.097
Anthrone	0.412	0.013	0.588	0.575
Phenylacetylene	0.428	0.000	0.572	0.572
α-Naphthylamine	0.434	0.000	0.566	0.566
Thio-β-naphthol	0.441	0.000	0.559	0.559
Biphenyl	0.458	0.000	0.542	0.542
Tetraphenylethylene	0.449	0.070	0.551	0.481
Diphenylamine	0.463	0.000	0.537	0.537
Benzoine	0.486	0.000	0.513	0.513
α-Nitronaphthalene	0.499	0.000	0.501	0.501
Triphenylamine	0.510	0.000	0.490	0.490
Triphenylene	0.544	0.000	0.456	0.456
Anthraquinone	0.573	0.000	0.426	0.426
Azobenzene	0.595	0.000	0.404	0.404
α-Naphthoquinone	0.662	0.000	0.338	0.338
α-Naphthol	0.691	0.000	0.309	0.309

TABLE 2. THE CONCENTRATIONS OF VARIOUS SPECIES AFTER IRRADIATION TO D_2

Additive	r/r_0	r_+/r_0	$1-r_+/r_0$ $-r/r_0$	A^+-left
p-Benzoquinone	0.138	0.315	0.545	0.088
Tetramethylphenylenediamine -2·HCl	0.000	0.346	0.653	0.072
Chrysene	0.000	0.120	0.879	0.027
Fluorene	0.017	0.039	0.942	0.006
2,3-Benzophenanthrene	0.083	0.000	0.916	0.000
3-Mehtylcholanthrene	0.123	0.006	0.870	0.000
Dibenzoanthracene	0.130	0.044	0.825	0.010
Hydroquinone	0.390	0.067	0.541	0.012
α-Nitroso-β-naphthol	0.446	0.169	0.383	0.068
trans-Stilbene	0.266	0.000	0.733	0.000
o-Terphenyl	0.288	0.000	0.711	0.000
Anthracene	0.281	0.000	0.718	0.000
β-Nitroso-α-naphthol	0.531	0.230	0.237	0.099
Styrene	0.430	0.000	0.569	0.000
Triphenylbenzene	0.415	0.000	0.584	0.000
Perylene	0.156	0.089	0.753	0.045
Phenanthrene	0.391	0.000	0.608	0.000
Pyrene	0.391	0.036	0.572	0.036
m-Terphenyl	0.430	0.000	0.569	0.000
Triphenylethylene	0.402	0.000	0.597	0.000
Naphthalene	0.452	0.000	0.547	0.000
p-Terphenyl	0.401	0.000	0.598	0.000
Diphenylpicrylhydrazine	0.190	0.177	0.631	0.142
Anthrone	0.539	0.003	0.457	0.010
Phenylacetylene	0.670	0.000	0.329	0.000
α-Naphthylamine	0.437	0.028	0.534	0.028
Thio-β-naphthol	0.539	0.000	0.460	0.000
Biphenyl	0.474	0.000	0.529	0.000
Tetraphenylethylene	0.345	0.000	0.654	0.000
Diphenylamine	0.468	0.051	0.531	0.051
Benzoine	0.562	0.000	0.437	0.000
α-Nitronaphthalene	0.395	0.000	0.604	0.000
Triphenylamine	0.639	0.000	0.360	0.000
Triphenylene	0.601	0.000	0.398	0.000
Anthraquinone	0.554	0.014	0.430	0.014
Azobenzene	0.663	0.000	0.336	0.000
α-Naphthoquinone	0.464	0.000	0.535	0.000
α-Naphthol	0.566	0.021	0.412	0.021

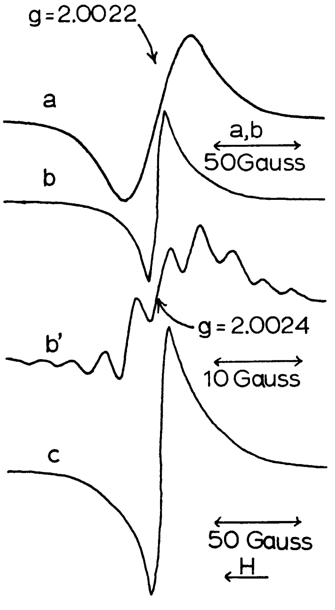

Fig. 1. a; PVC without additive irradiated to D_1.
b; PVC with perylene irradiated to D_1.
b′; the sample same as (b) but modulation width was 0.46 gauss.
c; PVC with perylene irradiated to D_2.
In all the spectra, modulation width employed was 8.0 gauss unless otherwise indicated.

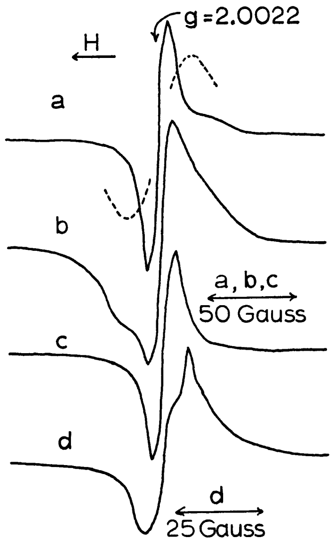

Fig. 2. a; PVC with hydroquinone irradiated to D_1. The dotted curve indicates a part of the spectrum same as Fig. 1a.
b; same as (a) irradiated to D_2.
c; PVC with *p*-benzoquinone irradiated to D_1.
d; same as (c) but modulation width was 0.5 gauss.

air before this spectrum was taken. Figures 3a and 3c indicate that, in these two isomers of nitrosonaphthol, the isotropic hyperfine splittings are somehow different.

Discussion

The primary radiation-chemical process in PVC is undoubtedly either an ionization or the formation of an excited state. Until now, the thermal-molecular and the thermal-segmental motions have generally been used to interpret the transporation of the excitation and the ionization in condensed phases as well as in the gas phase, and the kinetics governed by them. If, in some cases, the molecular motion-transportation theory was unsuccessful in explaining the kinetic data obtained, some inhomogeneous distribution of the primary, activated species, *e. g.*, a spur-like distribution, or some unknown impurities were assumed in order to solve such difficulties. In the present work it was found that the ESR of PVC can be totally converted to something else, or some 90% of it does not appear at all, if the PVC particles are coated with an aromatic additive. Benzene, used as the solvent for the additive, is not a solvent of PVC, and so it is very unlikely that additive molecules as large as 3-methylcholanthrene (5 rings with a methyl side chain) can uniformly penetrate into the segments of PVC. The additives are adsorbed only on the surface of polymer particles, probably by van der Waals adsorption. Therefore, it is definitely impossible to interpret the results obtained in this work if we limit the mechanism of the charge and excitation transporations to the molecular and the segmental motions.

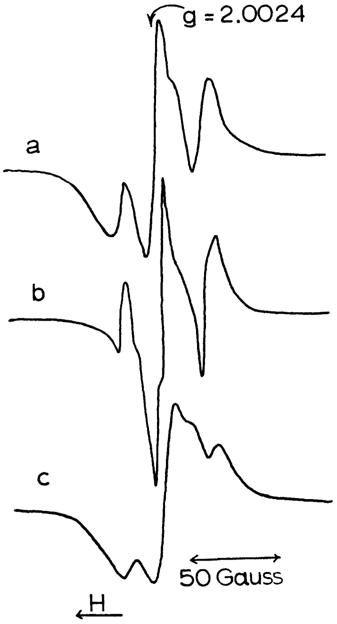

Fig. 3. a; PVC with α-nitroso-β-naphthol irradiated to D_1.
b; same as (a) but irradiated to D_2 and then bleached in air. The modulation width was 0.9 gauss.
c; PVC with β-nitroso-α-naphthol irradiated to D_1.

The radiation-chemical studies of alkyl halides and the systems in which an alkyl halide is the matrix or the solvent have almost established that an aromatic compound is converted to its cation, not to its anion, when it is supported in the alkyl halide matrix and irradiated by ionizing radiation.[6–10] In the present work, therefore, the most likely species for explaining the ESR spectra in Figs. 1, 2, and 3 are the cations of the additive molecules which coated the surface of PVC particles. Free radicals can be ruled out from the possible species for interpreting the spectra. If $\mathrm{PVC} \rightsquigarrow \mathrm{PVC'}\cdot + \mathrm{H}\cdot$ (or $\mathrm{Cl}\cdot$), which is a bond scission, occurs and if the atomic species formed jumps out of the PVC particle and adds to the aromatic hydrocarbon on the surface of the particle, A, to form AH·, both PVC′· (which should be identical with S·) and AH· will be observed in most of the cases studied. The hyperfine structure of the perylene-PVC spectrum in Fig. 1 also leads us to reject the idea of the existence of AH·. Since AH· has 13 hydrogen atoms, two of which are in the $>CH_2$ form, there cannot be any set of eight nearly-equivalent pairs of protons interacting with the unpaired electron.

Two effects of the additives adsorbed on the surface have been observed. One is the transformation of S· to the additive cation, and the other is the quenching of the precursors of S·, which otherwise generates S·. In the cases of diphenylpicrylhydrazine and *p*-benzoquinone, at the dose of D_1 most of the unpaired electrons were observed in the form of the additive cation. In the cases of fluorene, 2,3-benzophenanthrene, and 3-methylcholanthrene, the number of unpaired electrons observed was reduced to some 10% of the value obtained without an additive.

These results indicate that the activated species (ionic or excited) can conduct through a PVC particle. On the surface, this activation is transferred to the additive molecule by intermolecular interaction. After the transfer, the activated additive molecule can either be ionized or lose its energy by a radiative or a nonradiative deactivation to its ground state.

If the primary activated state of PVC described above is an excited state, to be written as P^{**}, it moves to the surface to become a surface excited species, P_s^{**};

$$P^{**} \longrightarrow P_s^{**},\ P_s^{**} + A \longrightarrow P_s + A^* \qquad (1)$$

which then may react with the adsorbed additive, A, to be deactivated to P_s. The P_s^{**} may also produce S·, whose nature is not yet known exactly. The excited additive, A^*, thus formed will be deactivated or ionized to A^+ and e^-, depending on the nature of the additive molecule:

$$A^* \longrightarrow A^+ + e^- \qquad (2)$$

$$A^* \longrightarrow A + (h\nu) \qquad (3)$$

Along with (2), the electron capture by PVC, P, takes place: $e^- + P \rightarrow P^-$. The amounts of S· and A^+ are shown in Table 1 and Table 2. The amount of (3) is equal to $(1-r_+/r_0-r/r_0)$ in the tables. $(1-r/r_0)$ in the tables indicates, then, the sum of the amounts of (2) and (3). In other words, $1-r/r_0$ in Table 1 indicates the total amount of energy going out of a PVC particle to the surface additives. $1-r/r_0-r_+/r_0$ in both tables indicates the total amount of energy which is dissipated by A^* by a radiative (with $h\nu$ in (3)) or by a non-radiative relaxation to the ground state. An alternate scheme, postulated by Ueda,[7] is also possible; in it (1) and (2) are replaced by the equation: $P_s^{**} + A \rightarrow P_s^- + A^+$.

A hole-conduction may also explain the phenomena. By irradiation, an excited ion, P^{+*}, may be formed. The P^{+*}, an energy-rich hole, may then move to the surface to form P_s^{+*}, which may then be transferred to the additive molecule:

$$P \rightsquigarrow P^{+*} + e^-$$

$$P^{+*} \longrightarrow P_s^{+*},\ P_s^{+*} + A \longrightarrow P_s + A^+ \qquad (1')$$

P_s^{+*} may also form S·;

$$P_s^{+*} \longrightarrow S\cdot \qquad (2')$$

The electron, which conducts more slowly than P^{+*} in this system,[6] will gradually come to the surface of the particle to recombine with A^+, which will create an excited state of A, which may then go to the ground state; on the other hand, if the electron affinity of A^+ is not larger than P, A^+ will stay stable on the surface. According to this scheme;

$$A^+ + e^- \longrightarrow A^* \longrightarrow A + (h\nu) \qquad (3')$$

$1-r/r_0$ in the tables is equal to the amount of (1′). So far as the present paper is concerned, there is no way to judge which is true, (1) or (1′), or whether or not both are true.

As is shown in Table 2, oxygen does not much affect the unpaired electrons found in additive molecules (see (A^+-left) in Table 2). This is good evidence that these species are cations and not anions, because an anion is very vulnerable to O_2. The unpaired electron left in pure (meaning without an additive) PVC after irradiation has been believed to be in the form of a free radical. However, the electric conductivity studies of irradiated PVC by Barnes *et al.*[11] have indicated that the unpaired electrons formed in irradiated PVC can be squeezed out if an electrostatic field and some thermal gradient is applied. Therefore, it is proper to say that no definite structure has been established for the paramagnetic species formed in irradiated PVC at room temperature.

Though the carbon atom has $2s2p^3$ sigma bonds, there can be $3s3p^3$ sigma orbitals and so on. Normally these additional "sigma orbitals" are not occupied by any electrons. However, if the $1s$ electron of a carbon atom is knocked off by a γ-photon, it may occupy the $3s3p^3$-sigma orbital, which is extended throughout the molecule. This excited state, P^{**}, $1s^1(2s2p^3)^{8/2}(3s3p^3)^{1/n}$, where 8/2 signifies the shared covalent bond and where $1/n$ signifies a bond extended to n-carbon atoms, would move quite quickly throughout the molecule or the polymer particles. Also, the P^{+*}, $1s^1(2s2p^3)^{8/2}$ hole can be expected to conduct. Though the $1s$ orbital radius of carbon atom is considerably smaller than the $2s2p^3$ sigma-bond radius, which decides the adjacent C–C bond distance in PVC, some overlap of adjacent $1s$ orbitals is possible if one of them includes only one electron. Therefore, the $1s$ unpaired spin (hole) may be exchanged between two adjacent carbon atoms.

It may be concluded that the cation or the excitation of PVC formed inside a particle penetrates through the particle toward the surface to form P_s^{+*} or P_s^{**}. Otherwise, 90% of the quenching of the unpaired electrons on the surface is impossible. Inside a particle, the molecular orbital or the unpaired electron will show some repulsive interactions with the normal sigma orbitals of other polymer segments or other molecules. On the surface, no such interaction exists; the ionized species can thus be said to be more stable than inside the particle.

In the present experiments, it seemed that the surfaces of PVC particles were saturated with the additive molecules. The overall efficiency of an additive, therefore, may be determined by the following four conditions:

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[11] J. E. Barnes, F. E. Hoeker, and L. Kevan, *Rad. Res.*, **40**, 235 (1969).

(a) the concentration of the additive on the surface (which is almost saturated with the additive) of the PVC particle; (b) the overlap integral between the wave functions of the additive orbitals and that of the surface of a PVC particle in the excited or the ionized state; (c) the energies required for the ionization or the excitation of the additive molecule, and (d) the relaxation rate constants of the excited states of the additive molecule on the surface of PVC. The values of (a) and (b) are not yet known, while those of (c) and (d) have been partly tabulated in several books.[12,13] There is an experimental method for ascertaining the values of (a), but the values of (b) will not easily be found. For this reason, at the present stage of our research, it is not possible to interpret the data in Table 1 and Table 2 in terms of the physical properties of each of the 38 additive compounds listed. It is hoped that the data presented in the tables nevertheless open a new possibility for the study, both in experiment and in theory, of the conduction and stabilization processes of the radiation-induced active centers in the condensed phases.

The authors wish to express their thanks to Dr. Sachiyuki Tominaga of the Mitsui Toatsu Chemical Co. for his kind suggestions in connection with this work.

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[12] J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley & Sons, New York, N. Y. (1967), p. 308.

[13] A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, New York, N. Y. (1962), p. 178.