

SENSITIZED FORMATION OF ION-RADICALS OF AROMATIC AMINES DURING RADIOLYSIS OF FROZEN ORGANIC GLASSES

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Fig. 1

Figure 1: Fig. 1

Abstract**Full Text****PHYSICAL CHEMISTRY****Kh. S. Bagdasar' yan, Z. A. Sinitsyna****SENSITIZED FORMATION OF ION-RADICALS
OF AROMATIC AMINES DURING RADIOL-
YSIS OF FROZEN ORGANIC GLASSES***(Presented by Academician N. M. Zhavoronkov, July 19, 1962)*

In a paper from our laboratory (¹), it was shown that upon γ -irradiation at the temperature of liquid nitrogen of methyl methacrylate films containing small additions of aromatic amines, cation-radicals of these amines are formed; these can be identified from their absorption spectra in the visible region. Formation of cation-radicals also occurs upon irradiation of these amines in a frozen hydrocarbon glass. The present paper reports the results of new investigations in this latter area.

The substance under study was dissolved in a mixture of isopentane and methylcyclohexane. The solution was freed from air by vacuum treatment and then transferred in vacuum into a quartz cell 0.5 cm thick. The cell was sealed off from the vacuum apparatus, frozen with liquid nitrogen, and subjected to γ -irradiation in a Dewar filled with liquid nitrogen. Only those solutions were used which, on freezing, gave transparent glasses. The dose rate was $4.1 \cdot 10^{15}$ eV/g \cdot sec. Spectrophotometry of the colored reaction products at the temperature of liquid nitrogen was carried out on an SF-4 spectrophotometer, the cell compartment of which had been adapted to accommodate a quartz Dewar with plane windows; inside it, on a special holder, the cell was mounted after irradiation. The holder made it possible to move the cell vertically, and the optical density was measured relative to liquid nitrogen.

Fig. 1. Dependence of the optical density at 670 $m\mu$ of an irradiated glass at -196° , containing 0.005 mole/l diphenylamine, on the dose.

Upon irradiation of a frozen glass containing 0.005 mole/l diphenylamine, a product is formed that colors the glass blue-green, with an absorption maximum at 670 $m\mu$. The optical density increases proportionally to the dose up to $7 \cdot 10^{18}$ eV/g and remains constant upon further increase of the dose (Fig. 1).

Figure 2 shows the dependence of the optical density of the colored products

Fig. 2

Figure 2: Fig. 2

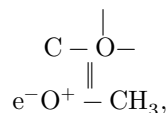
on the concentration of amine in the glass, at a dose of $7.3 \cdot 10^{18}$ eV/g. For diphenylamine and triphenylamine, the concentration of ion-radicals reaches a constant value at an amine concentration of 0.005 mole/l. On thawing of the glasses, the color rapidly disappears and, at the same time, a flash of blue luminescence is observed.

It follows from these experiments that, as in the case of methyl methacrylate films, the accumulation of amine cation-radicals is limited by a certain limiting concentration, which cannot be exceeded either by increas-

with increasing dose or by increasing the amine concentration. This limiting concentration evidently depends on the limiting concentration of electrons that can be retained in traps effective at liquid-nitrogen temperature. Experiments with triphenylamine make it possible to estimate the magnitude of this limiting concentration. As before ⁽¹⁾, we shall take for the absorption coefficient of the cation-radical of triphenylamine the same value as for tritolyamine, $1.1 \cdot 10^4$ ⁽²⁾. The optical density upon reaching the limiting concentration of cation-radicals is 0.080 (Fig. 2); consequently,

$$C = 0.080 / 1.1 \cdot 10^4 \cdot 0.5 = 1.5 \cdot 10^{-5} \text{ mol/l.}$$

This value is two orders of magnitude smaller than the limiting concentration of cation-radicals of triphenylamine in polymethyl methacrylate. This difference is evidently connected with the electron-acceptor properties of the ester group in the polymethyl methacrylate unit. If the ionic structure of the ester group is taken into account, addition of an electron to this group may be represented as follows:



These considerations make it possible to understand why, in the preceding work, we were unable to detect the formation of cation-radicals upon irradiation of amines in polystyrene films. It should be noted that the value found for the limiting concentration of cation-radicals represents a lower limit for the concentration of electrons, since part of the positive charge may exist in the form of positive ions of the substrate.

Fig. 2. Dependence of the optical density (at the absorption maximum) of irradiated glass at -196° , containing amines, on the amine concentration. 1 – diphenylamine, 2 – triphenylamine.

Fig. 3

Figure 3: Fig. 3

The limiting concentration of cation-radicals is reached at a dose of $7.3 \cdot 10^{18}$ eV/g and an amine concentration of 0.005 mol/l. Under these conditions the radiation yield of cation-radicals is 0.16, calculated per energy absorbed by the whole system. If only the energy absorbed by the amine is taken into account (electron fraction $1.2 \cdot 10^{-3}$), the yield is 135, which is 10 times greater than the energetically possible value 14 (ionization potential of amines $\simeq 7$ eV). Thus, the conclusion made earlier ⁽¹⁾ is confirmed: the formation of cation-radicals occurs not as a result of the direct action of radiation on the amines.

Fig. 3. Dependence of the optical density (at the absorption maximum) of irradiated glass at -196° , containing amines (0.005 mol/l) and CCl_4 , on the concentration of CCl_4 . 1 –diphenylamine, 2 –triphenylamine.

The above considerations are confirmed by the following experiments. The introduction of carbon tetrachloride greatly increases the yield of cation-radicals upon irradiation of diphenylamine (Fig. 3). This result can be explained by the electron-acceptor properties of carbon tetrachloride*. However, in this case too a saturation effect is observed at a CCl_4 concentration equal to 0.05 mol/l. From this one may conclude that only a small fraction of the CCl_4 molecules in the stationary state proves to be in

* In a recently published work ⁽³⁾ it is noted that addition of CCl_4 suppresses the formation of negative $\text{C}_{10}\text{H}_8^-$ ions upon irradiation of a frozen solution of naphthalene in tetrahydro-2-methylfuran, which is in good agreement with the data of our work.

in the form of negative ions. For a mixture containing 0.005 mol/l diphenylamine and 0.005 mol/l CCl_4 , increasing the dose from $7.3 \cdot 10^{18}$ to $29.2 \cdot 10^{18}$ eV/g does not change the concentration of cation radicals. It is interesting that the addition of CCl_4 does not affect the yield of cation radicals from triphenylamine. This fact as yet has no explanation.

When hydrocarbon glasses containing diphenylamine and triphenylamine are irradiated, only cation radicals of diphenylamine are formed, even in the case where the concentration of triphenylamine is three times greater than the concentration of diphenylamine. The optical density at 670 m μ decreases somewhat in the presence of triphenylamine; however, no increase in density is observed in the region of 640 m μ , characteristic of triphenylamine cation radicals (Fig. 4).*

Fig. 4. Absorption spectrum of glasses at -196° , containing amines. 1 –triphenylamine (0.005 mol/l), 2 –diphenylamine (0.005 mol/l), 3 –triphenylamine (0.005 mol/l) + diphenylamine (0.005 mol/l).

Fig. 4. Absorption spectrum of glasses at -196° , containing amines. 1 – triphenylamine (0.005 mol/l), 2 – diphenylamine (0.005 mol/l), 3 – triphenylamine (0.005 mol/l) + diphenylamine (0.005 mol/l)

Figure 4: Fig. 4. Absorption spectrum of glasses at -196° , containing amines. 1 – triphenylamine (0.005 mol/l), 2 – diphenylamine (0.005 mol/l), 3 – triphenylamine (0.005 mol/l) + diphenylamine (0.005 mol/l)

These experiments confirm the conclusion drawn that the formation of cation radicals does not occur as a result of the direct action of radiation on the amines, since in that case the formation of both types of cation radicals should be expected. It also follows from these experiments that the transfer of energy from the substrate to the amine (or hole migration) occurs directionally from the substrate to the amine possessing the greater electron-donor properties (diphenylamine).

Additives of anisole, tetrahydrofuran, and naphthalene at concentrations of 0.005 mol/l do not color the glass upon irradiation and do not affect the formation of diphenylamine cation radicals (0.005 mol/l).

The experiments described in the present and preceding communications open up interesting possibilities for systematic studies of electronic and ionic processes, as well as processes of energy migration in the condensed phase. At present these studies are being carried out in our laboratory in various directions.

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named after L. Ya. Karpov

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* R. I. Milyutinskaya in our laboratory found that, upon irradiation of a frozen film of polymethyl methacrylate containing 0.06 mol/l triphenylamine and 0.06 mol/l β -naphthylamine, only cation radicals of β -naphthylamine are formed, coloring the film pink (absorption maximum at 520 m μ).

Note: Figure translations are in progress. See original paper for figures.

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