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Abstract

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DETECTION OF HYDROGEN ATOMS IN ELECTRON PHOTOTRANSFER REACTIONS

During the last 15–20 years, a number of works $^{(1-4)}$ have advanced the supposition that free hydrogen atoms are formed in photochemical reactions in aqueous media according to reactions of the type:

$$M + H_2O + h\nu \rightarrow M^+ + OH^- + H\cdot \qquad (1)$$

The particle M may be metal ions of variable valence ($V^{+2}, Cr^{+2}, Mn^{+2}, Fe^{+2}, Co^{+2}, U^{+3}$, etc.), as well as various anions ($J^-, N_3^-, SH^-, SO_3^{2-}$, etc.).

The conclusion that process (1) occurs was made in all these cases on the basis of analysis of the chemical products of the reaction and investigation of the kinetic features of the process. In the work of Dainton and James $^{(2)}$ it was shown that the long-wavelength boundary of the spectral region in which process (1) takes place changes in parallel with the magnitude of the ionization potential of particle M. In the same work it was shown that, during photoinduced polymerization of acrylonitrile and methyl methacrylate due to photoionization of metal ions in D_2O, an atom of D is found in the terminal group of the polymer. This result is a weighty argument in favor of the assumption that, in the primary act of the photochemical reaction, a hydrogen atom is formed, which subsequently adds to a double bond. In a later work, however, these same authors $^{(4)}$ note a number of difficulties arising when polymerization is used as a method for studying phototransfer of electrons in the course of process (1).

As a result of the development of the method of electron paramagnetic resonance (e.p.r.), it is now possible to raise the question of investigating reaction (1) by directly detecting the hydrogen atoms formed in its course. Identification of hydrogen atoms by the e.p.r. method is facilitated by the fact that their spectrum, in the absence of any strong interaction with the medium, is a doublet with a splitting between the components of ~ 500 oersteds. No other radical or free atom can have such a spectrum.

In view of the high mobility and high reactivity of hydrogen atoms, reaction (1) had to be carried out under conditions ensuring stabilization of these particles.

Fig. 1 and Fig. 2: EPR spectra

Figure 1: Fig. 1 and Fig. 2: EPR spectra

For this purpose we decided to carry out measurements in the solid phase and at low temperatures. From the data available in the literature on irradiation it follows that in most frozen solids, including ice, hydrogen atoms readily diffuse even at a temperature of 77°K, and that, for their detection, it is necessary to work at hydrogen and helium temperatures (5). The only known exception to this rule is frozen aqueous acids, upon irradiation of which with γ-rays from Co^{60} at 77°K, considerable concentrations of hydrogen atoms can be detected (6).

Proceeding from this, we chose as the medium for our experiments frozen aqueous solutions of acids containing small amounts of $FeSO_4$.

and KJ. The samples were irradiated with ultraviolet light for one hour. A PRK-7 mercury lamp was used as the radiation source. The electron paramagnetic resonance signals were recorded using an EPR spectrometer described earlier (7).

Upon irradiation, at 77° K, of frozen solutions of $FeSO_4$ in dilute and concentrated H_2SO_4 and H_3PO_4 (the acid concentration was varied from ~40 to 96%), a doublet with a splitting of ~500 oersted was found in the spectrum. This result unambiguously proves the validity of the assumption concerning

Fig. 1. EPR spectra of hydrogen and deuterium atoms formed upon irradiation of the system
$FeSO_4 - D_2O - H_2SO_4$

Fig. 2. EPR spectra of hydrogen atoms and free radicals formed upon irradiation of the system
$C_6H_6 - H_2O - H_2SO_4$

the formation of free hydrogen atoms in electron phototransfer reactions. A similar spectrum, consisting of two components with the same splitting, was also observed upon irradiation of frozen KJ solutions in dilute H_2SO_4 and H_3PO_4. The role of particle M in this case was apparently played by the anion J^-, which is in agreement with the conclusions of work (2).

For a final verification of the conclusion that a reaction of type (I) occurs, experiments were carried out in solutions containing heavy water. In this case, in the spectrum, as is seen from Fig. 1, along with the doublet from hydrogen atoms, a triplet from deuterium atoms appeared ($i = 1$). The distance between neighboring components of the hyperfine structure of the EPR spectrum of deuterium atoms, in agreement with theory, is ~78 oersted.

It is also of interest to study the possibility of formation of hydrogen atoms upon irradiation with ultraviolet light of frozen aromatic systems. It is known that

Fig. 3 and Fig. 4: EPR spectra traces

Figure 2: Fig. 3 and Fig. 4: EPR spectra traces

polynuclear condensed aromatic molecules (anthracene, perylene, naphthacene, etc.) in concentrated sulfuric acid are readily ionized, giving positive ions—radicals ([8], [9]). Since the ionization potential of benzene is higher than that of these compounds, the ion—radical $C_6H_6{}^+$ is not formed in sulfuric acid. However, if additional energy is supplied to the reacting system in the form of a light quantum, one may expect that, also in the case of benzene, ionization will occur with simultaneous formation of a hydrogen atom by a process of type (I):

$$C_6H_6 + H_2O + h \rightarrow C_6H_6^+ + OH^- + H. \qquad \text{(I')}$$

$$C_6H_6 + H_3O^+ + h \rightarrow C_6H_6^+ + H_2O + H. \qquad \text{(II)}$$

Experiments carried out by us in the system C_6H_6 –H_2O –H_2SO_4 showed that, upon irradiation of benzene in aqueous and concentrated acid,

hydrogen atoms are indeed formed (Fig. 2). It is not possible to give an unambiguous interpretation of the central part of the spectrum (Fig. 2a and Fig. 3) on the basis of the data obtained. The four central components (marked by arrows in Fig. 3), having relative intensities close to the distribution $1:3:3:1$, are not saturated at the microwave powers used by us, whereas the outer components undergo quite noticeable saturation. This circumstance gives grounds for assigning these two spectra to two different radicals. The distinct multicomponent hyperfine structure of the central line, and also the fact that the total splitting of the central part of the spectrum (the quadruplet), $\Delta H \simeq 22$ oersteds, is close to the value characteristic of the anion $C_6H_6^-$ (10), makes it possible to conclude that this spectrum is due to a paramagnetic particle whose free valence is localized on the aromatic ring.* It may be said, however, that this particle cannot be an isolated positive ion—a radical—since its spectrum should consist of an odd number of components.

Fig. 3. Central part of the EPR spectrum of free radicals formed upon irradiation of the system C_6H_6—H_2O—H_2SO_4

Fig. 4. Components of the hyperfine structure of the EPR spectra of hydrogen atoms formed upon irradiation:
a –C_6H_6—H_2SO_4—H_2O,
b –$FeSO_4$—H_2SO_4—H_2O

The doublet (Fig. 2b) is of interest because of the very large magnitude of the splitting (~ 130 oersteds). A doublet with the same splitting is assigned in work (11) to the HCO radical. However, under our conditions it is difficult to suppose the formation of such a radical.

Attention should also be drawn to an interesting feature of the EPR spectrum of hydrogen atoms. As can be seen from Fig. 4, on both sides of the main component of the hyperfine structure of the spectrum of hydrogen atoms formed upon irradiation with ultraviolet light of the systems $C_6H_6—H_2O—H_2SO_4$ and $FeSO_4—H_2O—H_2SO_4$, weaker components are observed. These additional components can be attributed to the effect of rotation of the spins of protons in the molecules surrounding the hydrogen atom ([6,12]). Confirmation of such an interpretation may be provided by the closeness of the distance between the additional components (5 oersteds) to the distance corresponding to the proton-resonance frequency at the strength of the magnetic field used by us, $H = 3300$ oersteds.

* It is known from the literature (9) that the EPR spectra of positive and negative ion-radicals are very similar.

It is also necessary to note the phenomenon of saturation of the signal from hydrogen atoms. In our experiments with benzene, the lines of H atoms are strongly saturated; in experiments with Fe^{++}, however, this is not observed, which is apparently connected with the high concentration of paramagnetic ions with a short relaxation time.

A study of the phenomenon of saturation and of the character of the distribution of intensities between the main and side lines in the EPR spectrum of H atoms may make it possible to elucidate the specific features of their weak interactions with surrounding molecules and to approach the question of the distance between H atoms and the initial particle that gave up an electron under the action of light.

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