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ON THE PHOTOCHEMICAL REDUCTION OF FERRIC CHLORIDE IN AROMATIC HYDROCARBONS

(Presented by Academician A. N. Terenin, 19 XII 1960)

As is known, the solubility of ferric chloride in benzene and other aromatic hydrocarbons under ordinary conditions of moist air is extremely low. However, with careful removal of moisture it is possible to obtain dilute solutions of this salt in benzene (concentration on the order of 10^{-3} M), sufficiently stable under vacuum conditions. In the spectrum of these solutions a single absorption band was found, with a maximum at 340 mμ. It was suggested (1) that it corresponds to a "forbidden" transition from the ground singlet state of benzene to the lowest triplet state, the probability of which greatly increases owing to the perturbing action of the paramagnetic ferric chloride molecules. It is possible, however, to give another interpretation of the origin of this band, to which A. N. Terenin drew attention (2). Since the bond between the molecules $FeCl_3$ and C_6H_6 has a donor–acceptor nature, it is natural to consider that the absorption band in question belongs to the type of "charge-transfer spectra," analogous to the ultraviolet spectrum of complexes of iodine with aromatic hydrocarbons (3).

If this interpretation of the spectrum is correct, then one should expect that absorption by $FeCl_3 \cdot C_6H_6$ complexes of an ultraviolet-light quantum corresponding to the absorption band at 340 mμ should lead to a deeper, intracomplex electron transfer than that already present in the normal state. The band under consideration should thus correspond to the process of photoreduction of ferric chloride by benzene. The same photoprocesses should be observed in solutions of $FeCl_3$ in other aromatic hydrocarbons. At the same time, in the series of these hydrocarbons, depending on their electron-donor properties, a definite regularity should be observed both in the positions of the corresponding absorption bands and in the magnitude of the photochemical effect. Our study of the spectra of ferric chloride in benzene, toluene, and *n*-xylene, as well as of the action of ultraviolet light on these systems, confirmed these conclusions of the theory. The results of this investigation are briefly set forth in the present article.

The experiments were carried out with solutions degassed under high-vacuum conditions (for photochemical investigations) or prepared in a dry chamber (for

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

recording absorption spectra). The hydrocarbons used in the work were subjected to thorough purification and drying by the methods described in (4). The concentration of $FeCl_3$ in the solutions was determined spectrophotometrically at $\lambda 470$ mμ in the form of a complex with sulfosalicylic acid. Solutions were used that contained the iron salt in concentrations from $1 \cdot 10^{-4}$ to $8 \cdot 10^{-4}$ M. Absorption spectra were recorded in quartz cuvettes on an SF-4 photoelectric spectrophotometer. Irradiation was carried out with a PRK-7 mercury lamp through a cobalt light filter that isolated light of $\lambda 365$ mμ. The quantum yields of the photoreaction were determined by means of a uranyl oxalate actinometer.

The experiments showed that solutions of $FeCl_3$ in all the hydrocarbons possess, in the near ultraviolet, one broad absorption band of high intens-

···intensity. The maximum of this band, on going from benzene to its derivatives, shifts toward the long-wavelength side. The bands also somewhat extend into the visible region, and this accounts for the yellow-brown coloration characteristic of all such solutions. The corresponding spectra are shown in Fig. 1.* The values of $\varepsilon_{\max}$ for solutions in benzene, toluene, and *p*-xylene are, respectively, 6700, 6200, and 5600. These values were obtained without taking into account the dimerization of ferric chloride assumed by some authors. Figure 2 shows the dependence observed between the position of the absorption maxima of the corresponding bands and the ionization potentials of the hydrocarbon solvents. The values of the latter were taken from (5). The distinctly linear character of this dependence is connected with the donor function of the solvent in the corresponding intermolecular bond and may also be regarded as one of the proofs that the spectral bands of the corresponding complexes are due to intermolecular electron transfer according to the scheme

Fig. 1. Absorption spectra of ferric chloride: **1** –in benzene, **2** –in toluene, **3** –in *p*-xylene, **4** –in mesitylene

Fig. 2. Dependence of the position of the absorption maxima of ferric chloride solutions on the ionization potentials of the solvents. **1** –benzene, **2** –toluene, **3** –*p*-xylene, **4** –mesitylene

$$C_6H_6 \cdot FeCl_3 \overset{h\nu}{\rightleftarrows} C_6H_6^+ \cdot FeCl_3^-. \tag{1}$$

An even more convincing fact in favor of this is that absorption of a quantum corresponds to the photochemical process of reduction of ferric chloride in all the

Fig. 3

Figure 3: Fig. 3

cases considered. This is indicated, above all, by a decrease in the intensity of the absorption bands upon irradiation of deoxygenated ferric chloride solutions with monochromatic light of $\lambda 365$ mμ (Fig. 3a). At the same time, ferrous iron is formed and is readily detected in the solution after irradiation by reaction with *o*-phenanthroline.

It must be assumed that the system $C_6H_6^+ \cdot FeCl_3^-$, formed as a result of absorption of a light quantum, is unstable and has a certain probability of being converted both back into the initial products and according to the equation

$$C_6H_6^+ \cdot FeCl_3^- \rightarrow C_6H_5^{\cdot} + FeCl_2 + HCl. \tag{2}$$

The latter path leads to further development of the reaction. Obviously, the more strongly expressed the electron-donor properties of the hydrocarbon, the less

* For mesitylene, only the optical densities of one solution were determined. Therefore the data on light absorption in this solvent are given in arbitrary units.

probability of return of the reaction system (1) to the initial state. In accordance with this, the yield of the photochemical reaction should be all the greater.

Indeed, measurements of the quantum yields of the photoreduction reaction, carried out for $\lambda = 365$ mμ, gave the following values of γ (with respect to $FeCl_3$): for benzene $6.1 \cdot 10^{-2}$; for toluene $13.6 \cdot 10^{-2}$; for *n*-xylene $18.8 \cdot 10^{-2}$. These data are averages from several experiments. As individual experiments showed, the quantum yields change hardly at all with an increase in temperature from 20 to 40°. The low values of γ indicate that the probability of return to the initial state is very high in all the cases studied. The observed increase in yield in the series of the three systems studied is, as can be seen, in agreement with the decrease in the ionization potentials of the hydrocarbons.

Fig. 3. *a*—reduction of ferric chloride in benzene upon irradiation with $\lambda = 365$ mμ: 1—absorption curve before irradiation, 2—after 5 min irradiation, 3—after 23 min irradiation; *b*—reduction of ferric chloride in benzene under dark conditions: 1—absorption curve of the initial solution, 2—after 4.5 hours, 3—after 17 hours, 4—after 65 hours.

From the literature data it is known[6] that reduction of ferric chloride by aromatic hydrocarbons with simultaneous chlorination of the latter is also observed under dark conditions upon boiling. As follows, however, from the data presented in Fig. 3b, the rate of the dark reaction at room temperature is so low that it can be neglected in determining the quantum yields. On the other hand, it follows from these data that chlorination of aromatic hydrocarbons by ferric chloride could be significantly intensified by the action of light, provided favorable conditions for its use can be ensured.

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