Journal of Molecular Structure, 177 (1988) 309-315
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

UV-VIS ELECTROCHROMISM DUE TO PROTON TRANSFER

O.V. CHRANINA, F.P. CZERNIAKOWSKI and G.S. DENISOV

Yaroslavl Polytechnical Institute and Institute of Physics, Leningrad State University, Leningrad (U.S.S.R.)

(Received 14 September 1987)

ABSTRACT

A tautomeric equilibrium with proton transfer has been found for complexes of hydroxyanthraquinone dyes-aliphatic amines in low polarity solvents by UV and IR spectroscopy. The shift of this equilibrium in an external electric field has been observed by the method of electrochromism in the visible region. In a polystyrene matrix below the β-transition temperature the proton transfer is partially frozen.

INTRODUCTION

The influence of an electric field on chemical equilibrium has been studied by Eigen and co-workers [1] using the relaxation technique. At about the same time an extensive theoretical analysis of the field effect on equilibrium and processes of chemical relaxation was undertaken by Schwarz [2]. Many fast chemical reactions accompanied by a change of dipole moment can be studied by UV spectroscopy in an electric field of low frequency. The results of the successful application of such an approach are illustrated in refs. 3–5. The present article is devoted to the study of equilibrium systems, with proton transfer under the influence of an electric field, by means of electronic spectra.

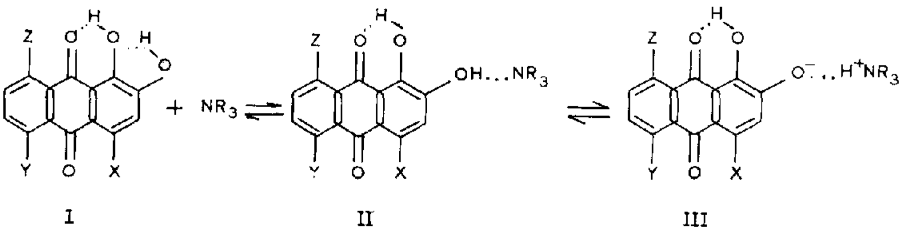
For the observation of the action of an electric field on chemical equilibrium, it is expedient to use electrochromism [6]. Electrochromism is a spectral method allowing the observation of changes in electronic spectra caused by the application of an audio-frequency electric field close to breakdown. Its sensitivity in electronic spectra with field modulation reaches 10^{-5}–10^{-6} units of absorbance. The spectrum of electrochromism is an increment of absorbance as a function of wavelength in the region of an absorption band.

The external electric field has a specific direction, which is important for molecules with a high dipole moment. Thus, for the study of chemical equilibrium in an external electric field proton transfer complexes were chosen. In these complexes, proton transfer is accompanied by an increase of the dipole moment up to ~ 10 D [7]. Proton transfer in the complexes is a unimolecular

0022-2860/88/$03.50

reaction and therefore diffusion processes do not disturb the mechanism under investigation. In proton transfer systems the shift of the equilibrium induced by the electric field is observed because the equilibrium constant for complexes oriented by the electric field in the direction of the field is somewhat higher than in the opposite direction. Thus, under the action of the field the proton transfer equilibrium shifts towards the reaction products possessing a higher dipole moment.

The complexes of hydroxyanthraquinone dyes (alizarin X = Y = Z = H, purpurin X = OH, Y = Z = H, alizarin bordeaux X = H, Y = Z = OH) as proton donors with aliphatic amines (triethylamine, trioctylamine, dimethylbenzylamine, dicyclohexylamine) as proton acceptors were chosen for study. The binary donor–acceptor systems, as well as their solutions in toluene, CCl_4, and dioxane, have been studied. According to refs. 8 and 9 the interaction of I with proton acceptors is accomplished through the β-hydroxy group. The existence of the unimolecular equilibrium II $\rightleftharpoons$ III is confirmed by comparison of electronic and vibrational spectra.



EXPERIMENTAL

The experimental procedure was the same as in refs. 10 and 11. Vibrational spectra were obtained with a UR-20 spectrophotometer and electronic spectra with the spectral unit KSVU-3. Dyes were recrystallized from hot toluene solution. Electronic spectra of samples in the electric field were measured in a 0.25 mm thickness cell with windows covered by a conductive layer on the setup described in ref. 6. The spectra of electrochromism were obtained at $\theta = (\widehat{\bar{e},\bar{F}}) = 55°$ and $90°$, where θ is the angle between the directions of the electric field of the probe optical beam ($\bar{e}$ is the unit vector) and of the external electric field $\bar{F}$. The value of the angle, $\theta = 55°$, was chosen with a view to excluding the orientation effects of the components of the equilibrium II $\rightleftharpoons$ III [6]. On the basis of Liptay's conception [12], an equation was derived describing the shift of the chemical equilibrium in the electric field [13]. The increment of absorbance, ΔA^F_{ch}, is quadratic in field strength, does not depend on the direction of light polarization and is connected with the dimensionless equilibrium constant K by:

$$\frac{\Delta A_{\mathrm{ch}}^{F}}{A} = \frac{B'}{9}\left(\frac{F}{kT}\right)^{2} \frac{K}{K+1}\left[\mu_2^2 - \mu_1\mu_2 \cos(\widehat{\boldsymbol{\mu}_1,\boldsymbol{\mu}_2})\right] \tag{1}$$

Here F is the strength of the external field, $\boldsymbol{\mu}_1$, $\boldsymbol{\mu}_2$ the dipole moments of ionic and molecular forms of complexes, k is the Boltzmann constant, T is absolute temperature, and B' is a constant (see ref. 12).

RESULTS AND DISCUSSION

In Fig. 1, the electronic spectra of alizarin solution in toluene in the presence of excess dicyclohexylamine at different temperatures (290–340 K) are presented. The 430 nm band belongs to molecular form II of the complex, the 540 nm band to ionic form III. With increase of temperature the equilibrium II$\rightleftharpoons$III shifts to the left, all temperature changes being completely reversible. At the concentrations used only the complexes of stoichiometric composition 1:1 ex-

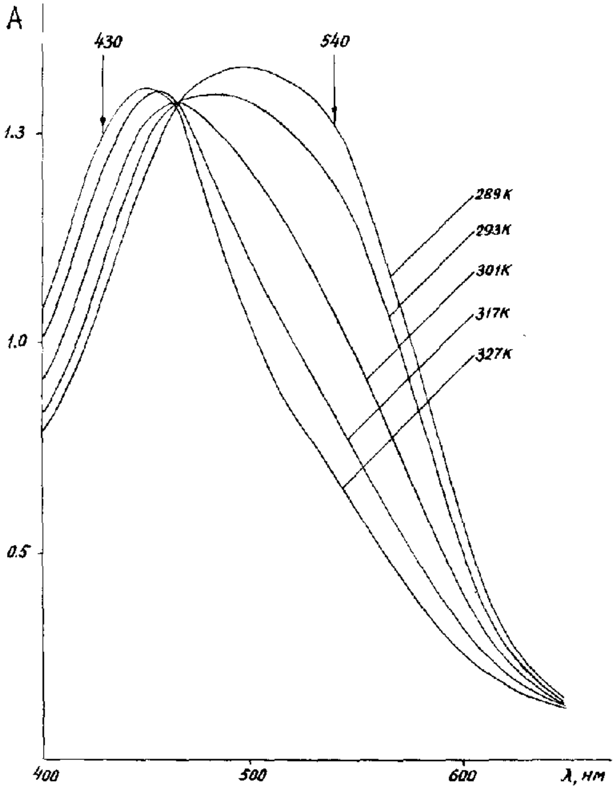


Fig. 1. Electronic spectra of solution of alizarin 3.43×10^{-3} M and dicyclohexylamine 3.43×10^{-1} M in toluene at different temperatures, $d = 1.065$ mm.

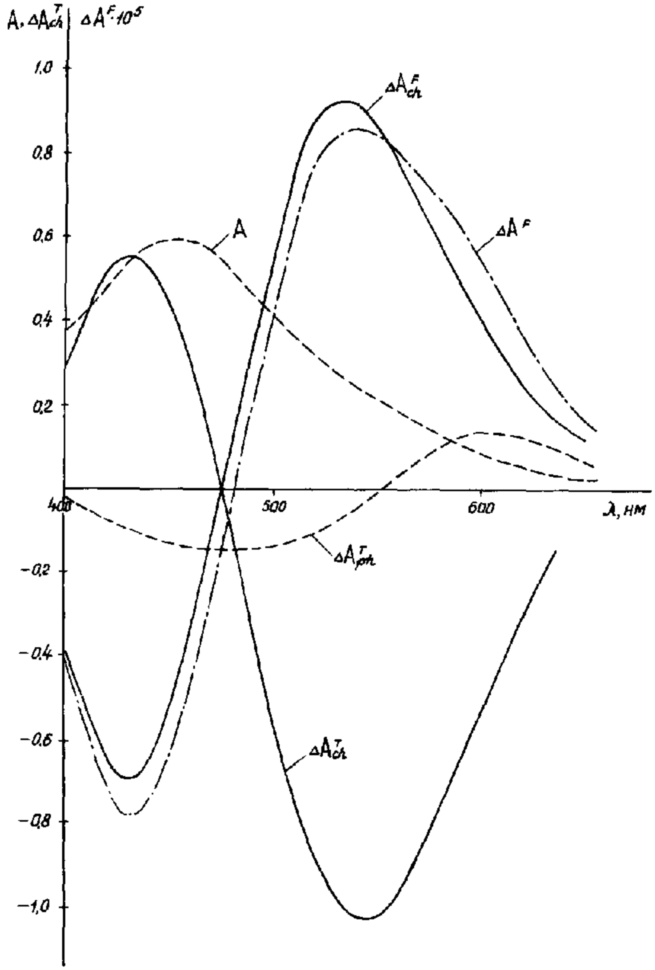


Fig. 2. Electronic spectrum A and the differences of absorption, caused by temperature ΔA^T_{ch} ($d = 1.065$ mm) and by the action of an electric field ΔA^F, ΔA^F_{ch}, ΔA^F_{ph} ($d = 0.25$ mm) for solution of alizarin and triethylamine in toluene; $T = 298$ K, $\theta = 55°$.

ist. The position of tautomeric equilibrium depends on the proton donating power of the dyes, the basicity of the amines and the temperature. Thermodynamic parameters of the proton transfer process for hydroxyanthraquinone–amine complexes lie within the intervals: $\Delta H^\circ = -(10\text{–}40)$ kJ M^{-1}, $\Delta S^\circ = -(50\text{–}100)$ J deg^{-1} M^{-1}.

The dipole moments of the complexes in the ground state were measured by the method of electrochromism, the directions of electronic transition moment being taken into account. The values obtained for the molecular form of dye–amine complexes are 2.3–2.8 D; for the ionic form 5.7–5.8 D [14, 15].

The spectra of the system with proton transfer equilibrium in the external electric field are shown in Fig. 2. The spectrum ΔA^F is presented as the sum of the two terms $\Delta A^F_{\mathrm{ch}} + \Delta A^F_{\mathrm{ph}}$, where ΔA^F_{ch} is the chemical contribution arising from the field-induced shift of proton transfer equilibrium and ΔA^F_{ph} is the physical effect, caused by the orientation polarization of ionic form of the complex [6]. The spectra, ΔA^T_{ch} (the difference of absorbance caused by temperature) and ΔA^F_{ch} were compared by plotting ΔA^T_{ch} versus ΔA^F_{ch} in different points of the 400–550 nm region. A satisfactory correlation dependence exists between these quantities (the correlation coefficient is 0.988), hence the profiles of $\Delta A^F_{\mathrm{ch}}(\lambda)$ and $\Delta A^T_{\mathrm{ch}}(\lambda)$ practically coincide. This confirms the idea that both spectra are caused by the same phenomenon, i.e. by the shift of tautomeric equilibrium as a result of factors such as electric field and temperature. However, this type of intensity change of spectral bands is only a particular case of spectral manifestation of the field-shift of chemical equilibrium. It is typical for cases when $\gamma < 55°$ ($\gamma = (\widehat{\boldsymbol{\mu}, \mathbf{m}})$ is the angle between the dipole moment of the complex in the ground state, $\boldsymbol{\mu}$, and the transition moment with unit vector $\mathbf{m}$ for both forms II, III). Different values of angles γ can give rise to a great variety of deformations of electronic spectra observed in an electric field [15].

According to eqn. (1), a linear dependence should exist between the relative change of absorbance and the factor $K/(1+K)$. It has been found that the experimental dependencies $\Delta A^F_{\mathrm{ch}}/A$ versus $K/(1+K)$ for the ionic band of complexes of alizarin, purpurin and alizarin bordeaux are described by straight lines in the interval $0.25 < K < 0.47$. The equilibrium constant for each system was varied as a result of temperature change from 290 to 340 K. It can be seen as confirmation of the correctness of the model used and also proves that the observed effects are caused by the field-induced shift of tautomeric equilibrium. On the basis of eqn. (1), the parameter cos $(\widehat{\mu_1, \mu_2})$, i.e., the angle between the dipole moments of the molecular and ionic forms, was estimated. For tautomeric complexes of alizarin and alizarin bordeaux with aliphatic amines, this angle was found to be about 130°, and for purpurin–amine complexes about 100°.

An attempt was made to use electrochromism for the study of the reorganization of a solvation shell of the tautomeric complex. It has been shown [16–19] that the necessary condition of unimolecular proton transfer is the appropriate scale of molecular mobility of surroundings of the complex. In particular, in polymeric media the shift of the equilibrium $\mathrm{II} \rightleftharpoons \mathrm{III}$ on cooling of the sample slows down near the temperature of β-transition corresponding to the freezing of the orientation mobility of polymeric chains. Hence, in high viscosity media the frequency of reversible proton transfer is controlled by the time of structural relaxation of a solvation shell.

The hydroxyanthraquinone dye–amine complexes in polystyrene show the phenomenon of partial freezing of proton transfer equilibrium near and below the temperature of β-transition, as noted previously [19]. The spectra of elec-

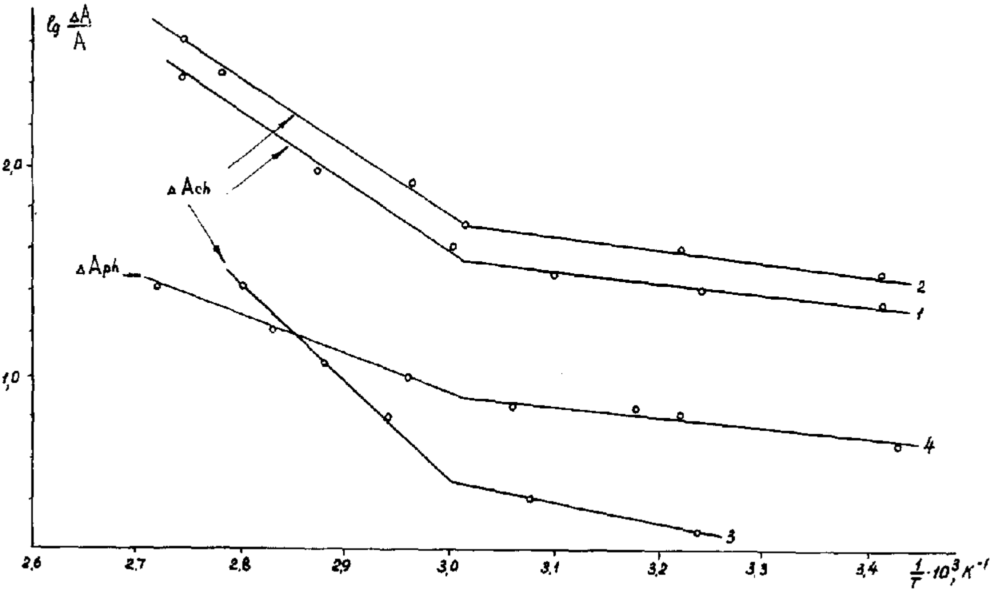


Fig. 3. Temperature dependence of log $\Delta A/A$ for the complexes with dicyclohexylamine of alizarin (1) and alizarin bordeaux (2); of purpurine with dimethylbenzylamine (3) ($\theta=55°$) and for the azo dye ($\theta=90°$) in polystyrene (4).

trochromism of these samples give qualitatively new information which supports this concept. In Fig 3, the dependencies of $\log(\Delta A^{F}_{\mathrm{ch}}/A)$ on $1/T$ are presented for tautomeric complexes at $\theta=55°$ (curves 1–3) and, for comparison, the dependence of the value $\log(\Delta A_{\mathrm{ph}}/A)$ at $\theta=90°$ is also given (curve 4), characteristic for the orientation polarizability of an azo dye as a probe [6]. In both cases the inflexion interval is in the vicinity of the β-transition temperature of the polymeric matrix.

CONCLUSIONS

The results obtained in this study demonstrate the efficiency of the method of electrochromism for investigations involving molecules with high dipole moments, and also for researching the influence of the medium on the kinetics of intracomplex proton transfer.

REFERENCES

1 V.K. Bergman, M. Eigen and L. De Maeyer, Ber. Bunsenges. Phys. Chem., 67 (1963) 819.
2 G. Schwarz, J. Phys. Chem., 71 (1967) 4021.
3 A. Persoons and M.V. Beylen, Pure Appl. Chem., 51 (1979) 887.
4 E. Neumann, Studia Biophys., 94 (1983) 107.

5 M. De Maeyer, P. Wolschann and L. Hellemans, in W.J. Gettins and E. Wyn-Jones (Eds.), Technique and Applications of Fast Reactions in Solution, 1979, Reidel, Dordrecht, p. 501.
6 F.P. Czerniakowski, Itogi Nauki Tekn, Ser. Biofiz., 15 (1983) 140 pp.
7 H. Ratajczak and L. Sobczyk, J. Chem. Phys., 50 (1969) 556.
8 G. Gillet, Bull. Soc. Chim. Fr., 8 (1966) 2624.
9 A.A. Tulub, E.E. Yudovich and V.V. Palchevsky, Vest. Leningr. Univ., 22 (1979) 70.
10 N.S. Golubev, G.S. Denisov and V.M. Schreiber, in N.D. Sokolov (Ed.), Vodorodnaja Svaz, 1981, Nauka, p. 212.
11 A.N. Delnov and G.S. Denisov, Zhur. Prikl. Spektrosk. U.S.S.R., in press.
12 W. Liptay, in E.C. Lim (Ed.), Excited States, Vol. I, 1974, Academic Press, p. 129.
13 G.S. Denisov, V.A. Krasheninnikov, O.V. Chranina and F.P. Czerniakowski, Deposit. U.S.S.R., 1987, in press.
14 O.V. Chranina, G.S. Denisov and F.P. Czerniakowski, Zhur. Fiz. Chim. U.S.S.R., 60 (1986) 2079.
15 G.S. Denisov, A.I. Kornilov, O.V. Chranina and F.P. Czerniakowski, Zhur. Fiz. Chim. U.S.S.R., 61 (1987) 1390.
16 A.I. Kulbida and V.M. Schreiber, Dokl. Akad. Nauk U.S.S.R., 250 (1980) 889.
17 M. Rospenk, I.G. Rumynskaya and V.M. Schreiber, Zhur. Prikl. Spektrosk. U.S.S.R., 36 (1982) 756.
18 G.V. Gusakova, G.S. Denisov and A.L. Smolyansky, Chim. Fiz. U.S.S.R., 4 (1985) 534.
19 G.S. Denisov, A.I. Kulbida, Z.Z. Rechapov, A.L. Smolyansky and V.M. Schreiber, Chim. Fiz. U.S.S.R., 1 (1982) 221.