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Heavy Atoms as Molecular Probes in Studying the Solvent Dependence of the Dynamics of Triplet Exciplexes.

U. STEINER and G. WINTER (*)

Institut für Physikalische Chemie der Universität Stuttgart
Pfaffenwaldring 55, *D*-7000 *Stuttgart* 80, *BDR*

Summary. — Electron transfer reactions between thiopyronine triplet (acceptor $^3A^+$) and the electron donors (D), aniline, *p*-Br-aniline and *p*-I-aniline, are investigated by flash spectroscopy in solvents of different viscosity and polarity. Due to the heavy-atom effect the radical yield becomes very sensitive to the solvent influence, which can be explained by the dynamic properties of a triplet exciplex ($^3(AD^+)$) formed as a primary product in the reaction between acceptor triplet and donor. Whereas on variation of solvent viscosity the solvent cage effect on the dissociation of $^3(AD^+)$ is observed, a change in solvent polarity is suggested to affect the radiationless deactivation of $^3(AD^+)$ to the ground state of the components.

1. – Introduction.

In polar solvents the quenching of excited states due to electron transfer reactions usually leads to the formation of radical ions. In the case of excited singlet states it has been demonstrated (1,2) that even in very polar solvents the formation of radical ions may occur via dissociation of an intermediately

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(1) K. SCHULTEN, H. STAERK, A. WELLER, H.-J. WERNER and B. NICKEL: *Z. Phys. Chem. N. F.*, **101**, 371 (1976).

(2) N. ORBACH and M. OTTOLENGHI: *Chem. Phys. Lett.*, **35**, 175 (1975).

formed exciplex detectable by its characteristic fluorescence. There is no reason why exciplexes should not be intermediates in the corresponding reactions of excited triplet states too. One cannot hope, however, to detect their phosphorescence if their lifetime amounts to a few nanoseconds only.

Here we report on the use of an indirect method for obtaining information on triplet exciplexes formed as intermediates in electron transfer reactions with dye triplets in polar solvents. The method is based on our observations (³) concerning the influence of halogen substituents on the radical yield in the electron transfer reaction between the thionine triplet (electron acceptor, ${}^3A^+$) and the monohalogen-substituted anilines (electron donors, D_X, X symbolizing the halogen substituent).

Our results (³) provided evidence for a mechanism represented by scheme I with the following implications:

$$\begin{tikzcd} {}^3A^+ + D_X \arrow[r] & {}^3(AD_X^+) \arrow[r, "k_{fr}"] \arrow[d, "k_{isc}"] & A\cdot + D_X^{+}\cdot \\ & A^+D_X & \end{tikzcd} \qquad \text{(scheme I);}$$

i) radical formation occurs via the intermediate (radical-pair–like) triplet exciplex ${}^3(AD_X^+)$;

ii) the radical yield is given by eq. (1):

$$\Phi_r = \frac{k_{fr}}{k_{fr} + k_{isc}}\,; \tag{1}$$

iii) the exciplex dissociation rate constant k_{fr} is approximately independent of the halogen substituent X and its position;

iv) the intersystem crossing rate constant k_{isc} of the triplet exciplex is determined by two factors:

$$k_{isc} = F_{el} \times F_{FC}\,, \tag{2}$$

where F_{FC}, the Franck-Condon factor, is insensitive to the substituent X and F_{el}, the electronic factor, is determined by the spin-orbit coupling constant (ζ_X) of the halogen substituent and the Hückel spin density ($c^2(\mathrm{pos}_X)$) at the position of X:

$$F_{el} \propto \zeta_X^2\, c^2(\mathrm{pos}_X)\,. \tag{3}$$

(³) U. Steiner and G. Winter: *Chem. Phys. Lett.*, **55**, 364 (1978).

2. – The concept of the probe function of heavy-atom substituents.

Though the Franck-Condon factor F_{FC} and the dissociation rate constant k_{fr} are approximately substituent-independent parameters of the triplet exciplex, the heavy-atom substituent effect on the electron factor F_{el} turns out to be a very useful tool in studying, *e.g.*, solvent influences on k_{fr} and F_{FC}. This is demonstrated in fig. 1, where we plot the radical yield, given by eq. (1), as a function of F_{FC}/k_{fr}, using a logarithmic scale and treating F_{el} as a constant parameter. In this way we obtain identical but horizontally displaced S-shaped curves, their relative shift being determined by the electronic factor F_{el}. If we assume that a certain solvent change leads to a change in the exciplex behaviour corresponding to a change of F_{FC}/k_{fr} from *a* to *b* (see fig. 1), the diagram clearly shows that the effect on the radical yield depends on the electronic actor, *i.e.* on the kind and position of the halogen substituent. Thus, by a suitable choice of X, determining F_{el}, the radical yield can be made a most sensitive measure of changes in F_{FC} and k_{fr}, which are substituent independent fand describe rather general properties of this type of exciplexes. It is in this sense that we regard the halogen substituents as probes for the dependence of the exciplex behaviour on external parameters.

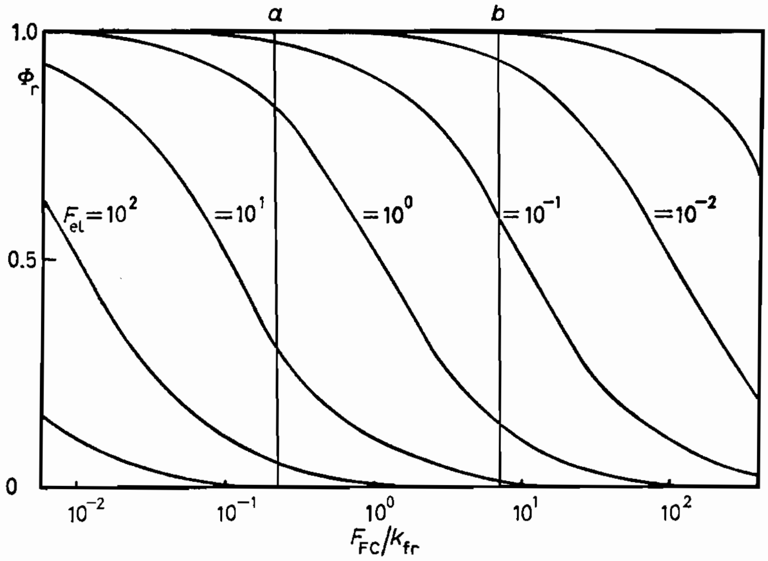

Fig. 1. – Radical yield Φ_r (eq. (1)) as a function of log (F_{FC}/k_{fr}) with F_{el} as a constant parameter.

In this paper we describe the use of such probes to detect the influence of solvent viscosity and solvent polarity on the behaviour of triplet exciplexes formed between thiopyronine triplet and aniline, *p*-bromoaniline and *p*-iodoaniline, respectively. The radical yield Φ_r per triplet molecule quenched by D_X was determined by microsecond flash spectroscopy. The method is described in ref. (⁴). For detailed information on the photochemical behaviour of thiopyronine and the absorption spectrum of the dye and its photochemical intermediates see ref. (⁵,⁶).

3. – Viscosity dependence.

The solvent viscosity was varied by using a series of mixtures of methanol and ethylene glycol, so that the polarity of the solvent was fairly constant over the whole series. Figure 2 shows the radical yield obtained with the different donors as a function of solvent viscosity. The radical yield decreases with increasing solvent viscosity due to the solvent cage effect on the exciplex dissociation. It is to be noted, however, that the viscosity effect is greatly enhanced by the heavy-atom substituents. This observation is completely accounted for by assuming the same viscosity dependence of k_{fr} in the corresponding exciplexes and by the probe function of the heavy-atom substituents as defined in fig. 1.

We can construct a diagram of this type, if we know k_{fr} in each solvent and assume F_{FC} to be viscosity independent. Adopting *p*-bromoaniline as a standard, we can obtain relative values of k_{fr} for each solvent viscosity by plotting the radical yields with *p*-bromoaniline on a standard S-curve as in fig. 3. Now we can plot the radical yield for the other donors at the corresponding positions and, as can be seen, in fig. 3 these points can be well fitted by the same type of S-shaped curves, the relative shifts being due to the different spin-orbit coupling (F_{el}) in the respective systems.

The radical yield may be extrapolated to zero viscosity by plotting $1/\Phi_{\text{r}}$ against the viscosity, since straight lines are obtained (fig. 4). An interpretation of slope and intercept of these can be given based on eq. (1). From eq. (1) and fig. 4 we infer

$$\frac{1}{\Phi_{\text{r}}} = 1 + \frac{k_{\text{isc}}}{k_{\text{fr}}} = a + b\eta\,. \tag{4}$$

Setting

$$\frac{1}{k_{\text{fr}}} = \tau_{\text{diss}} = \tau^0_{\text{diss}} + \text{const} \times \eta\,, \tag{5}$$

where τ^0_{diss} is the dissociation lifetime at zero viscosity, we obtain

$$a = 1 + k_{\text{isc}}\tau^0_{\text{diss}} \tag{6}$$

(⁴) U. Steiner, G. Winter and H. E. A. Kramer: *J. Phys. Chem.*, **81**, 1104 (1977).

(⁵) M. Morito and S. Kato: *Bull. Chem. Soc. Jpn.*, **42**, 25 (1969); F. Gollmick and H. Berg: *Photochem. Photobiol.*, **16**, 125, 471 (1972).

(⁶) G. Winter: Ph. D. Thesis, University of Stuttgart (1978).

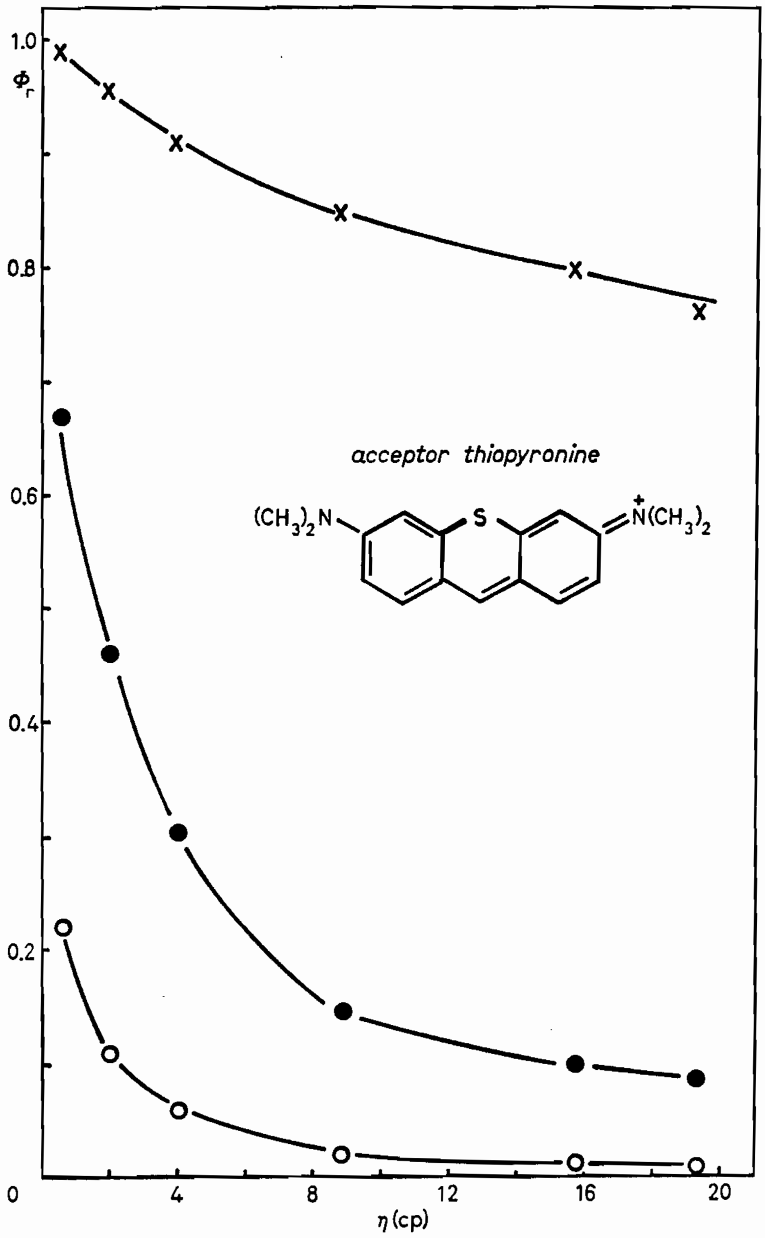

Fig. 2. – Radical yield Φ_r obtained under conditions of complete quenching of thiopyronine triplet by different electron donors as a function of solvent viscosity: ○ *p*-I-aniline, ● *p*-Br-aniline, × aniline.

and

$$b = \text{const} \times k_{isc}. \tag{7}$$

It is seen that the heavy-atom effect on k_{isc} enhances both slope and intercept. The quantity $a - 1$ is proportional to the dissociation lifetime of the exciplex at zero viscosity and may be regarded as a measure of the exciplex bonding forces. The quantity $1/\Phi_r - 1$ can be regarded as a relative measure of the effective dissociation lifetime due to exciplex bonding and solvent cage

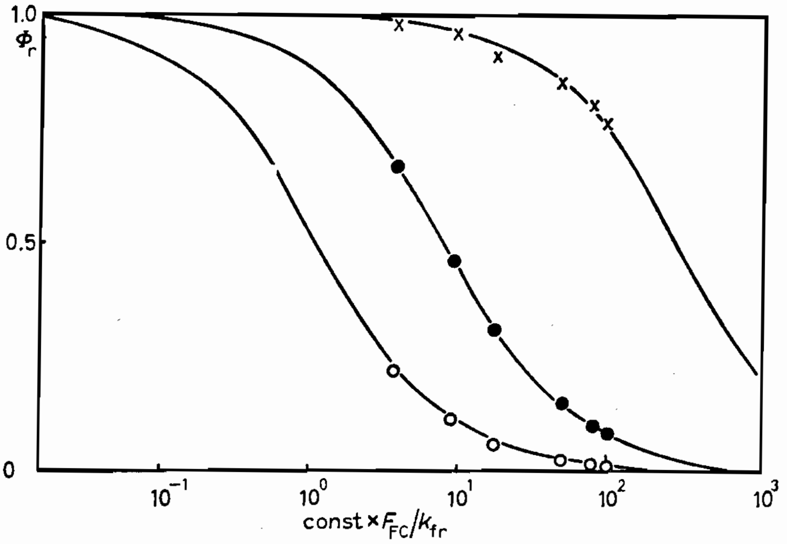

Fig. 3. – Radical yield Φ_r as a function of log (F_{FC}/k_{fr}) varied by solvent viscosity: o *p*-I-aniline, • *p*-Br-aniline, × aniline.

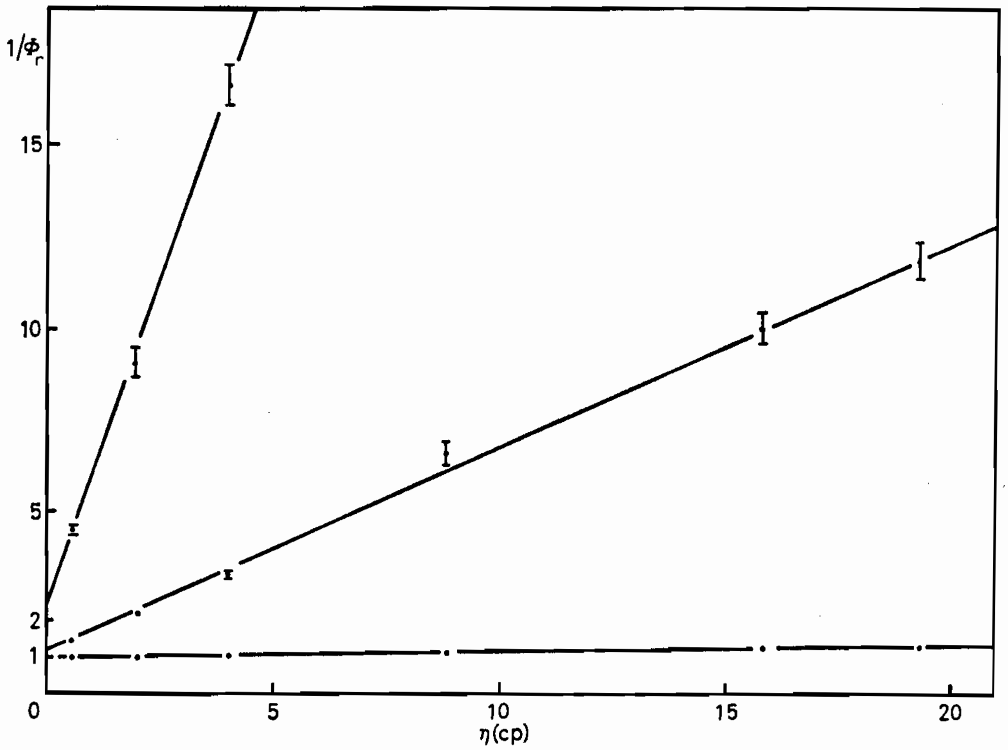

Fig. 4. – Extrapolation of $1/\Phi_r$ to zero viscosity. Straight lines in the order of increasing slope correspond to triplet exciplexes with aniline, *p*-bromoaniline and *p*-iodoaniline.

effect. The straight lines obtained for the heavy-atom substituted donors show that in a solvent of the viscosity of, *e.g.*, methanol ($\eta = 0.59$ cp) the cage effect has already increased the pure bonding dissociation lifetime by a factor of about 2.

4. – Polarity dependence.

For a variation of solvent polarity mixtures of acetonitrile and water or methanol and water were used. Due to the cationic dye only fairly polar solvents were applicable. The polarity effect on the radical yield is shown in fig. 5 for the various electron donors. Kosower's Z-value (7) was used as a measure of solvent polarity. As in the case of viscosity the polarity effect, too, is drastically enhanced by the heavy-atom substituents. The probe function diagram (fig. 6) is constructed in the same way as described above. Again we use the results for the p-bromoaniline to define the abscissa values for the different solvent compositions.

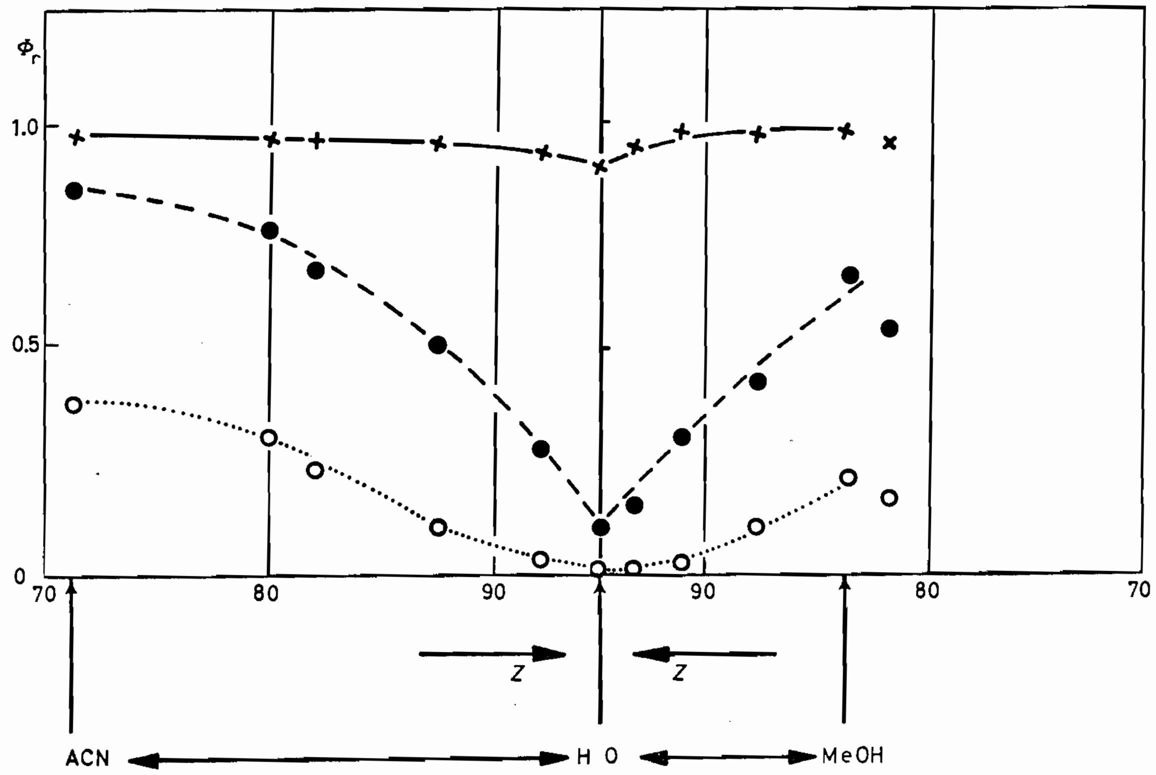

Fig. 5. – Radical yield Φ_r obtained under conditions of complete quenching of thiopyronine triplet by different electron donors in solvent mixtures of varying polarity (ACN acetonitrile, MeOH methanol, NMF N-methyl-formamide), Z is Kosower's polarity parameter (7): ○ p-I-aniline, ● p-Br-aniline, × aniline.

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(7) E. W. Kosower: *An Introduction of Physical Organic Chemistry* (New York. N. Y., 1968).

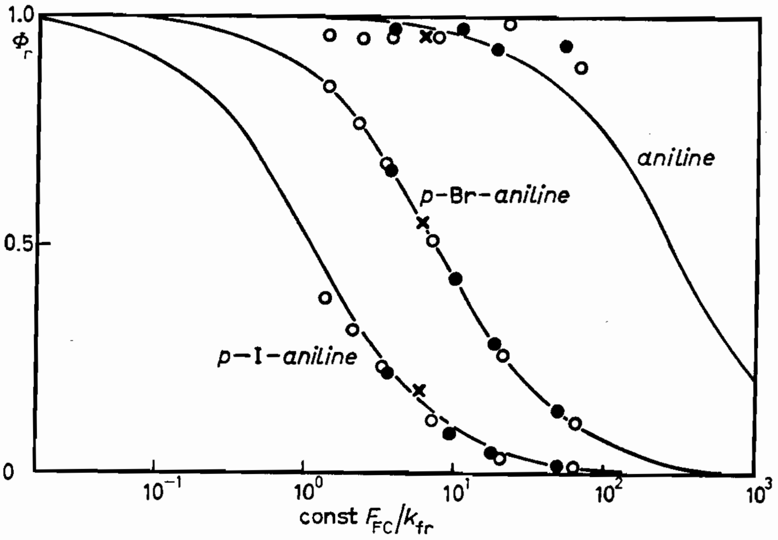

Fig. 6. – Radical yield Φ_r as a function of log (F_{FC}/k_{fr}) varied by solvent polarity. Solvents: o ACN-H_2O, • MeOH-H_2O, × NMF.

As can be seen from fig. 6, the shifted S-curves obtained for aniline and *p*-iodoaniline from the viscosity variation experiments (fig. 4) give a good fit in the case of polarity variation too. Thus it appears that the solvent effect proper on F_{FC}/k_{fr} is independent of heavy-atom substitution and the electronic factors F_{el} are in the same ratio as in fig. 4.

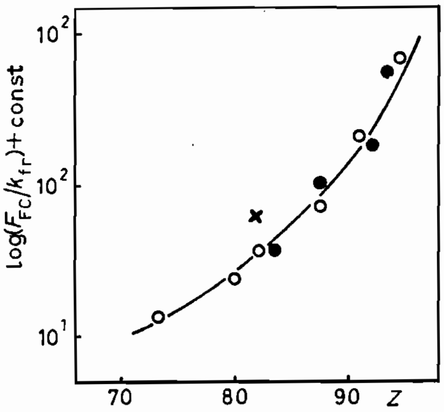

Fig. 7. – Log (F_{FC}/k_{fr}) as a function of solvent polarity parameter Z (7). For indication of solvent composition see fig. 6.

In fig. 7 log (F_{FC}/k_{fr}) is plotted as a function of the solvent polarity parameter Z. The diagram shows that F_{FC}/k_{fr} is a unique function of this solvent parameter, independent of the solvent composition used (if F_{FC}/k_{fr} is plotted as a function of the solvent DK different lines are obtained for acetonitrile/water or methanol/water mixtures).

So far the analysis of the results has shown that the ratio F_{FC}/k_{tr} is solvent polarity dependent. Since no charges are separated when the exciplex dissociates (see scheme I), k_{tr} should bear no significant polarity dependence. Hence the polarity dependence observed should be due to F_{FC}. We suggest the following explanation: since the intersystem crossing is combined with a back transfer of an electron from the acceptor to the donor molecule, a solvent reorganization will take place after the electronic process (fig. 8). The solvent polarity dependence of the resolvation energy (⁸) renders the electronic energy gap polarity dependent and hence the Franck-Condon factor should increase with increasing solvent polarity.

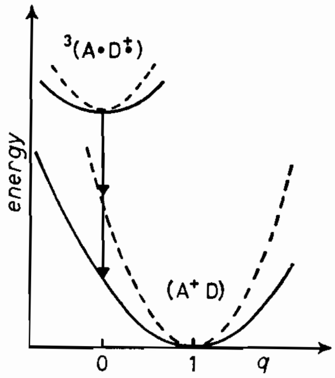

Fig. 8. – Energy of exciplex and ground-state encounter pair as a function of solvent orientation parameter q, corresponding to equilibrium solvation of the hypothetic charge distribution (A^qD^{1-q}): ——— less polar solvent, — — — more polar solvent.

(⁸) R. A. Marcus: *J. Chem. Phys.*, **24**, 966 (1956).

● RIASSUNTO (*)

Si **analizzano** le **reazioni di** trasferimento **di** elettroni tra i tripletti di tiopironina (accettore $^3A^+$) e i donatori di elettroni (D), anilina, *p*-Br-anilina e *p*-I-anilina con la spettroscopia mediante flash in solventi con diversa viscosità e polarità. Per l'effetto degli atomi pesanti la resa di radicali diventa molto sensibile all'influenza del solvente che può essere spiegata dalle proprietà di eccipleso a tripletto ($^3(AD^+)$) che si forma come prodotto primario nella reazione tra il tripletto dell'accettore e il donatore. Mentre al variare della viscosità del solvente si osserva l'effetto gabbia del solvente sulla dissociazione di $^3(AD^+)$, si suggerisce che un cambiamento nella polarità del solvente influenzı la disattivazione priva di radiazioni di $^3(AD^+)$ fino allo stato fondamentale dei componenti.

(*) *Traduzione a cura della Redazione.*

Тяжелые атомы, как молекулярные зонды, при исследовании зависимости динамики триплетных эксиплексов от свойств растворителя.

Резюме (*). — Используя спектроскопию в растворителях с различной вязкостью и полярностью, исследуются реакции переноса электрона между триплетом триопиронина (акцептор $^3A^+$) и электронными донорами (D): анилином, *p*-Br-анилином и *p*-I-анилином. Вследствие влияния тяжелых атомов, выход радикалов является очень чувствительным к действию растворителя, что может быть объяснено динамическими свойствами триплетного эксиплекса $\left(^3(AD^+)\right)$, образованного, как первичный продукт, в реакции между акцепторным триплетом и донором. В то время, как при изменении вязкости растворителя наблюдается влияние решетки растворителя на диссоциацию $^3(AD^+)$, предполагается, что изменение полярности растворителя влияет на безызлучательную дезактивацию $^3(AD^+)$ в основное состояние компонент.

(*) *Переведено редакцией.*