

Evidence for the Marcus Inverted Region of Back-electron-transfer in Solution by means of Chemically Induced Dynamic Nuclear Polarization

Heinz G. O. Becker,* Dietmar Pfeifer and Klaus Urban

Sektion Chemie, Technische Hochschule 'Carl Schorlemmer', DDR-4200 Merseburg, German Democratic Republic

In order to detect the Marcus inverted region in electron-transfer reactions in solution it is more appropriate to follow not the forward but the back reaction. This can be done by means of chemically induced dynamic nuclear polarization, measuring the polarization of re-formed educts. The ^{13}C -CIDNP enhancement factors $V(^{13}\text{C})$ of re-formed arene diazonium salts in the photochemical electron transfer from singlet-excited rubrene to a series of *para*-substituted benzene diazonium tetrafluoroborates in chloroform have been determined. On plotting $V(^{13}\text{C})$ against the standard free reaction enthalpies of the back-electron-transfer, bell-shaped behaviour of the Marcus type is obtained. Taking the reorganizational energy ($\lambda = 0.81$ eV) from the maximum of this curve the Franck-Condon factors $F_{\text{FC}} = \exp(-\Delta G^\ddagger/RT)$ were calculated according to the Marcus quadratic equation, which, on plotting against $V(^{13}\text{C})$, give a linear correlation. The Franck-Condon factors (0, 2, ..., 1) show that the back-electron-transfer proceeds with nearly the theoretical maximum value k_0 .

The Marcus theory of electron-transfer reactions predicts a bell-shaped curve when the logarithms of electron-transfer rate constants k_e are plotted over the standard free reaction enthalpies ΔG° . The rate decrease in the region of strongly negative ΔG° values ('Marcus inverted region') has been the subject of many discussions, but is now experimentally firmly verified in rigid systems containing the electron-donor and acceptor groups at fixed distances.^{1,2} It appears that the electron transfer in these systems takes place preferentially by through-bond interaction.^{1,3} Rigid systems are, therefore, not a good model for reactions of freely diffusing reactants. In fact, information about the Marcus inverted region in solution is scarce. It may well be that in highly reactive systems with strongly negative ΔG° values the reaction distance of the forward-electron-transfer adjusts itself according to the reactivity of the system, *i.e.* that in the distance probability function $P = C \exp(-ar)$ the factor a depends on ΔG° , *i.e.* on the reorganizational energy λ .⁴

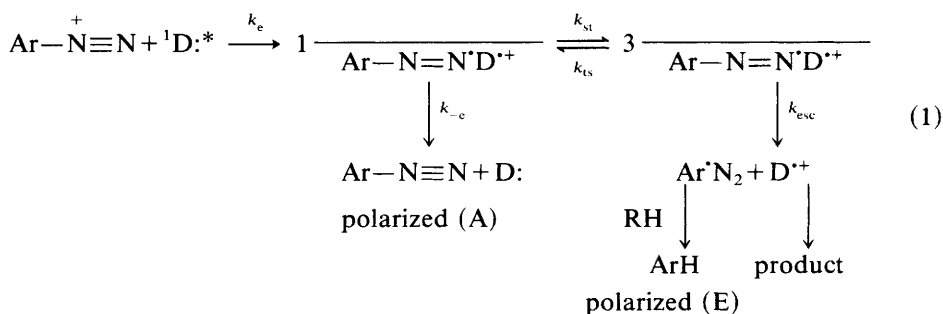
In order to verify the existence of the Marcus inverted region it seems more promising to look not at the forward reaction but at the back-electron-transfer which is kinetically first order and possibly simpler in its distance probability than the forward reaction [see ref. (5)]. In fact, extracting the back-electron-transfer from the electron-transfer kinetics by means of a kinetic model, Ohno and coworkers found⁶ that the Marcus inverted region also exists in solution. We obtained similar results when studying electron-transfer reactions with arene diazonium salts.⁷ Unfortunately, these results are based on a kinetic model with its inherent problems and pitfalls. We felt, therefore, that it is more reliable to use a method which directly reflects the back-electron-transfer. This is fundamental

to chemically induced dynamic nuclear polarization (CIDNP). According to the theory of CIDNP the probability, P , of recombination is

$$P \approx \int_0^{\infty} f(\text{molecular dynamics}) \times g(\text{spin dynamics}) \times \exp(-kt) dt.$$

Within a reaction series and at constant reaction conditions, the molecular dynamics $f(\eta)$ (dependence on viscosity) and the spin dynamics $g(|\alpha\rangle)$ and $g(|\beta\rangle)$ (dependence on hyperfine interactions of magnetically active nuclei) can be assumed constant. Thus, only the reactions dynamics $\exp(-kt)$ varies, and the CIDNP enhancement factors should reflect the dependence of the back-electron-transfer rates on the Franck-Condon factors between the pertinent energy hypersurfaces.

The reaction series studied was the photochemical dediazonation of *para*-substituted arene diazonium salts in the presence of rubrene (ArH) as electron donor:



D: = rubrene

Experimental

The arene diazonium tetrafluoroborates were synthesized according to standard procedures.

The photo-CIDNP spectra were taken under the following conditions: arene diazonium salt 1.0 mol dm^{-3} , rubrene $0.133 \text{ mol dm}^{-3}$, 18-crown-6 1.33 mol dm^{-3} , in chloroform containing 30 vol% CDCl_3 as lock substance. Irradiation within the probe was through a quartz rod with a high-pressure Hg lamp, $\lambda_{exc} > 460 \text{ nm}$ (filter C. Zeiss, GG14). A broad-band decoupled $^{13}\text{C}\{-^1\text{H}\}$ pulse Fourier transform technique was used; pulse angle $4.5 \mu\text{s}$, pulse separation 2 s, 150 scans (Bruker spectrometer HX-90-R). The CIDNP enhancement factors were determined from the integrated signals under illumination (I) and in the dark (I_0 , no CIDNP effects): $V(^{13}\text{C}) = (I - I_0)/I_0$.

Results and Discussion

The details of the analogous photo-CIDNP effects with pyrene as electron donor have already been published.⁸ In the present case rubrene ($E_{1/2}^{\text{ox}} = 0.90 \text{ V vs. SCE}$) was used as the donor instead of pyrene ($E_{1/2}^{\text{ox}} = 1.20 \text{ V vs. SCE}$) because the latter, owing to its resulting higher radical pair energy, gives no CIDNP effect with *p*-diethylaminobenzenediazonium salt. To obtain the formulated singlet electron transfer, high concentrations of reactants had to be used, which, in the case of rubrene, was not possible when using acetonitrile as the solvent. Thus, the reaction was performed in chloroform in the presence of 18-crown-6 to obtain sufficient solubility of the diazonium salts used. It was shown by an independent experiment that the crown ether does not act as an electron-transfer reagent.

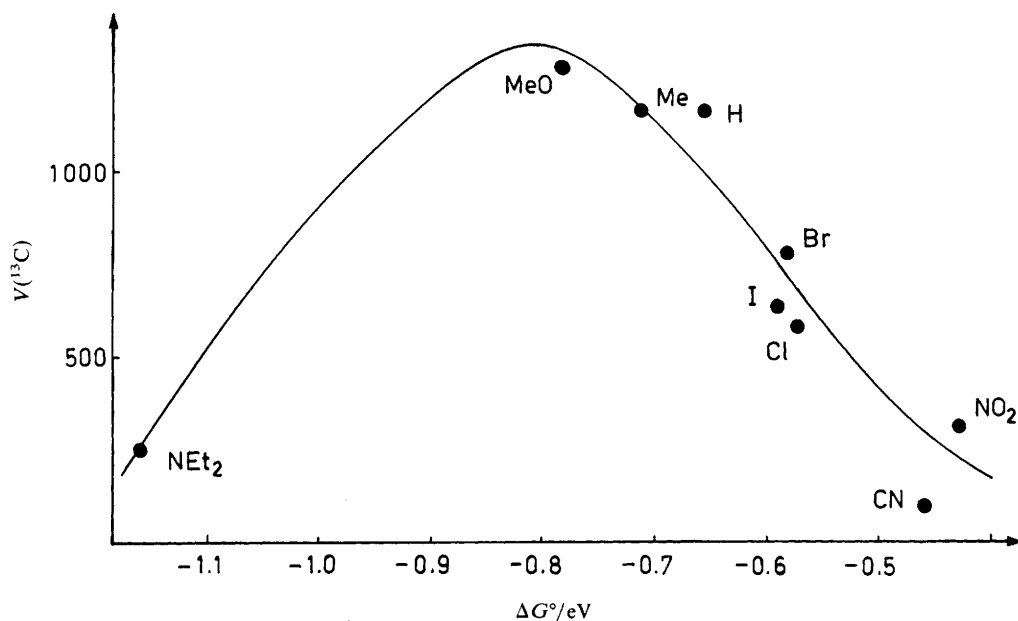


Fig. 1. Dependence of ^{13}C -CIDNP enhancement factors of re-formed arenediazonium salts on the radical pair energies during the photochemical electron transfer from singlet-excited rubrene to *p*-substituted benzenediazonium tetrafluoroborates in chloroform. The solid curve represents the (normalized) Franck-Condon factors according to eqn (5a).

In all experiments total absorption by rubrene was maintained. From simple thermodynamic considerations it follows that the electron transfer k_e proceeds for all compounds in the reaction series in a diffusion-controlled manner, *i.e.* each encounter leads to reaction. The dediazonium quantum yield $\Phi = k_e / (k_e + k_{-e})$ is, therefore, determined only by k_{-e} .

To obtain direct information about the back-electron-transfer k_{-e} the CIDNP effects of the re-formed diazonium compounds (enhanced absorption) were measured. Since the back-electron transfer is a fast first-order reaction the 'fast' ^{13}C -CIDNP variant (due to the high hfs constant of ^{13}C) was used. In this case a measurable polarization develops after a few nanoseconds [see ref. (8b)]. The CIDNP enhancement factors are plotted in fig. 1 *versus* ΔG° of the back-electron-transfer reaction.

$$\Delta G^\circ = -E_{\text{rp}} = E_{1/2}^{\text{ox}}(\text{rubrene}) - E_{1/2}^{\text{red}}(\text{ArN}\equiv\text{N})^+ \quad (2)$$

The $E_{1/2}^{\text{red}}(\text{ArN}\equiv\text{N})^+$ values were taken from ref. (9). Fig. 1 shows Marcus-type behaviour in spite of the moderately negative ΔG° values. Note that similar results were obtained in ref. (8b), but in this case the reaction conditions were not sufficiently standardized to allow such a correlation. The CIDNP enhancement factors for the recombination polarization are defined by the efficiency of back-electron-transfer under the influence of α - and β -nuclear spins, respectively:

$$V_{\text{CIDNP}} \approx \eta_{-e}^{|\alpha\rangle} - \eta_{-e}^{|\beta\rangle} \quad (3)$$

$$V_{\text{CIDNP}} \approx \frac{1}{1 + \frac{k_{\text{esc}}}{k_{-e}} f(\eta) g(|\alpha\rangle)} - \frac{1}{1 + \frac{k_{\text{esc}}}{k_{-e}} f(\eta) g(|\beta\rangle)} \quad (4)$$

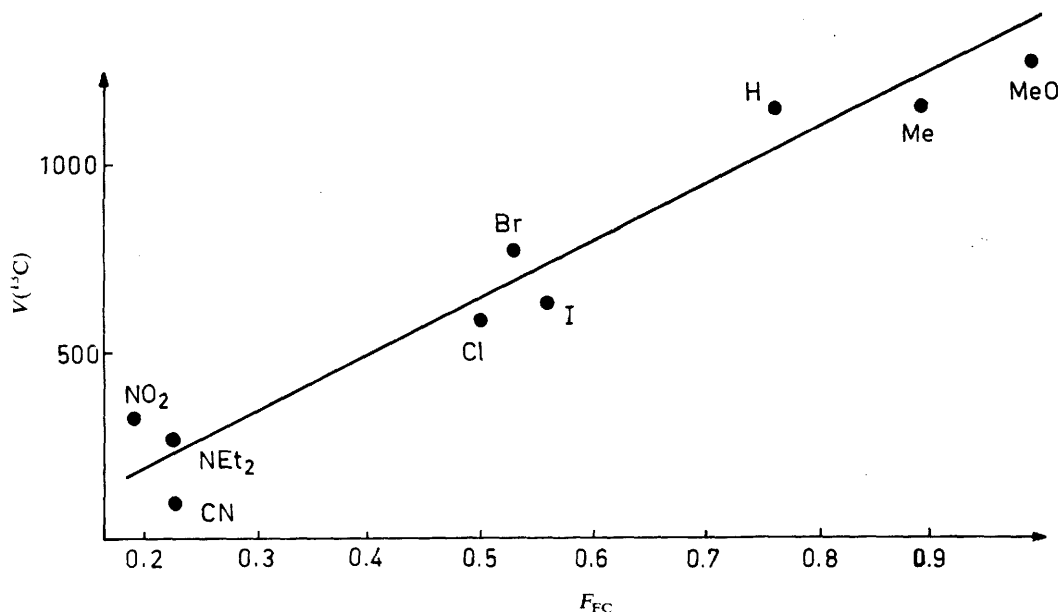


Fig. 2. Linearization of the ^{13}C -CIDNP enhancement factors from fig. 1 according to eqn (5).

The aryldiazo radicals are σ -radicals with a spin density distribution $N_\alpha : N_\beta \approx 2:1$. Therefore, the radical electron interacts strongly with substituents in the *meta* position of the arene ring but negligibly with substituents in the *para* position [see ref. (8), (10)]. Thus, the *para* substituents used in the present reaction series have no influence on the spin dynamics, and the functions $f(\eta)g(|\alpha\rangle)$ and $f(\eta)g(|\beta\rangle)$ in eqn (4) can be considered constant throughout the series. Similarly, heavy-atom effects are absent, as shown by the position of Cl, Br and I in fig. 1 and 2. The CIDNP enhancement factors reflect, therefore, only the chemical dynamics of the back-electron-transfer. Unfortunately, there are no substituents available to close the big gap of substituent effects between *p*-MeO and *p*-NEt₂.†

If the curve in fig. 1 really reflects Marcus behaviour, linearization should be possible according to the adiabatic or non-adiabatic approximation of electron-transfer processes:

$$k_{-e} = k_0 \exp(-\Delta G^\ddagger/RT) = k_0 \exp\left(-\frac{\lambda}{4} \left[1 + \frac{\Delta G^\circ}{\lambda}\right]^2 / RT\right) \quad (5a)$$

$$= k_0 F_{\text{FC}}$$

$$k_e = \frac{2\pi}{\hbar} |H_{\text{AB}}|^2 F_{\text{FC}} \quad (5b)$$

†From $E_{1/2}^{\text{red}}$ or Hammett substituent constants can be seen that there are no substituents known which fit into the region between *p*-MeO and *p*-R₂N. *p*-NH₂ or *p*-NHR diazonium salt are stable only in the diprotonated form (otherwise triazenes are formed); the protonated amines are no longer electron donors but have substituent constants in the vicinity of *p*-NO₂. *p*-OH would be a suitable substituent, but *p*-hydroxybenzene diazonium salt exists in the pH region of our experiments in the zwitterionic form (*p*-quinone diazide). The tacitly assumed, reasonable and necessary precondition that the solvent reorganizational parameter λ remains constant throughout the whole reaction series would be no longer fulfilled for *p*-quinone diazide. The experiments described in ref. (8b) with pyrene as electron donor in acetonitrile showed the maximum of CIDNP enhancement factors for *p*-chlorobenzene diazonium salt, and *p*-H, *p*-Me and *p*-MeO substituted benzenediazonium salts are located already on the Marcus inverted branch. This is a further proof that the curve of fig. 1 in the present paper is correct in its shape.

ΔG° is defined by eqn (2) and λ is the reorganizational energy. The Franck-Condon factor is expressed by the exponential term of eqn (5a).

According to the Marcus theory the rate maximum of electron transfer corresponds to $\Delta G_0 = -\lambda$ and consequently $\Delta G^\ddagger = 0$. Taking $\lambda = 0.81$ eV from fig. 1 (optimized value to give the best straight line in fig. 2), and the radical pair energies ($R_p = -\Delta G^\circ$) the Franck-Condon factors were calculated and plotted against the CIDNP enhancement factors, cf. fig. 2.

In this representation the substituents are more evenly distributed over the curve. The linear dependence obtained confirms the Marcus-type behaviour. In a similar way, the (normalized) Franck-Condon factors when plotted *versus* ΔG° , give the solid curve drawn in fig. 1. Since the exponential term in eqn (5a) amounts in the present case to 0.2–1.0, the rate constants of back-electron-transfer nearly reach the maximum theoretical value k_0 . If k_0 amounts to *ca.* 10^{11} , as in the forward-electron-transfer, the rate constants of back-electron-transfer are in the present case in the range of 10^{10} – 10^{11} s⁻¹, which seems reasonable. These high values are probably due to the rather low reorganizational energies in the low-polarity solvent as compared to $\lambda = 2.1$ eV for the electron transfer from zinc phthalocyanine tetrasulphomorpholide to 4-methoxy-benzenediazonium tetrafluoroborate in acetonitrile.¹¹

References

- 1 G. L. Closs, L. T. Calcaterra, N. J. Green, K. W. Penfield and J. R. Miller, *J. Phys. Chem.*, 1986, **90**, 3673 and earlier papers.
- 2 M. R. Wasielewski, M. P. Niemczyk, W. A. Svec and E. B. Pewitt, *J. Am. Chem. Soc.*, 1985, **107**, 1080.
- 3 J. W. Verhoeven, *Pure Appl. Chem.*, 1986, **58**, 1285; N. S. Hush, M. N. Paddon-Row, E. Cotsaris, H. Oefering, J. W. Verhoeven and M. Heppener, *Chem. Phys. Lett.*, 1985, **117**, 8.
- 4 R. Marcus and P. Siders, *J. Phys. Chem.*, 1982, **86**, 622.
- 5 D. S. Brunschwig, S. Ehrenson and N. Sutin, *J. Am. Chem. Soc.*, 1984, **106**, 6855.
- 6 T. Ohno, A. Yoshimura and N. Mataga, *J. Phys. Chem.*, 1986, **90**, 3295. See also I. R. Gould, D. Ege, S. L. Mattes, S. Farid, *J. Am. Chem. Soc.*, 1988, **110**, 7242 and references cited therein.
- 7 H. G. O. Becker and S. Schulze, unpublished.
- 8 (a) H. G. O. Becker, D. Pfeifer and R. Radeaglia, *Z. Chem.*, 1977, **17**, 439; (b) H. G. O. Becker, D. Pfeifer and R. Radeaglia, *Z. Naturforsch., Teil b*, 1983, **38**, 1591.
- 9 M. P. Noskova, Zh. Belitskaya, I. L. Bagal and B. A. Porai-Koshits, *Reakt. Sposobnost Org. Soedin.*, 1971, **8**, 1025; H. Boettcher, A. V. El'tsov and N. I. Rtishchev, *J. Prakt. Chem.*, 1973, **315**, 725.
- 10 E. Gey, R. Radeaglia, H. G. O. Becker and D. Pfeifer, *Z. Chem.*, 1986, **26**, 405.
- 11 H. G. O. Becker, R. Krüger and R. Schütz, *J. Prakt. Chem.*, 1986, **328**, 729.

Paper 9/00595A; Received 8th February, 1989