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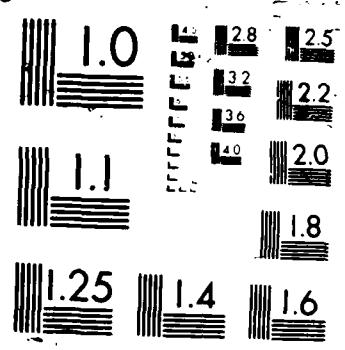
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AD-A190 146

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Contract N00014-86-K-0556

Technical Report No. 78

Solvent Relaxation in Thermal Electron-Transfer Reactions:
Some Comparisons with Real-Time Measurements of
Solvation Dynamics

by

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Prepared for Publication

in

Chem. Phys. Lett.

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February 17, 1988

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REPORT DOCUMENTATION PAGE

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|--|---|---|------------------------|
| 1a REPORT SECURITY CLASSIFICATION Unclassified | | 1b RESTRICTIVE MARKINGS | |
| 2a SECURITY CLASSIFICATION AUTHORITY | | 3 DISTRIBUTION / AVAILABILITY OF REPORT Approved for public release and sale; its distribution is unlimited. | |
| 2b DECLASSIFICATION / DOWNGRADING SCHEDULE | | | |
| 4 PERFORMING ORGANIZATION REPORT NUMBER(S) Technical Report No. 78 | | 5 MONITORING ORGANIZATION REPORT NUMBER(S) | |
| 6a NAME OF PERFORMING ORGANIZATION Purdue University Department of Chemistry | 6b OFFICE SYMBOL (if applicable) | 7a NAME OF MONITORING ORGANIZATION Division of Sponsored Programs Purdue Research Foundation | |
| 5c ADDRESS (City, State, and ZIP Code) Purdue University Department of Chemistry West Lafayette, IN 47907 | | 7b ADDRESS (City, State, and ZIP Code) Purdue University West Lafayette, IN 47907 | |
| 8a NAME OF FUNDING / SPONSORING ORGANIZATION Office of Naval Research | 8b OFFICE SYMBOL (if applicable) | 9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER | |
| 8c ADDRESS (City, State, and ZIP Code) 800 N. Quincy Street Arlington, VA 22217 | | 10 SOURCE OF FUNDING NUMBERS | |
| | | PROGRAM ELEMENT NO | PROJECT NO |
| | | TASK NO | WORK UNIT ACCESSION NO |
| 11 TITLE (Include Security Classification) Solvent Relaxation in Thermal Electron-Transfer Reactions: Some Comparisons with Real-Time Measurements of Solvation Dynamics | | | |
| 12 PERSONAL AUTHOR(S) G. E. McManis and M. J. Weaver | | | |
| 13a TYPE OF REPORT Technical | 13b TIME COVERED FROM _____ TO _____ | 14 DATE OF REPORT (Year, Month, Day) February 17, 1988 | 15 PAGE COUNT |
| 16 SUPPLEMENTARY NOTATION | | | |
| 17 COSATI CODES | | 18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number) | |
| FIELD | GROUP | solvent relaxation, electron transfer, time-resolved fluorescence ← | |
| | | | |
| 19 ABSTRACT (Continue on reverse if necessary and identify by block number) The role of solvent dielectric relaxation on the barrier-crossing dynamics for outer-sphere electron transfer (ET), as evaluated from the solvent-dependent kinetics of metallocene self-exchange reactions, is compared with recent real-time measurements of polar solvation dynamics obtained from time-dependent fluorescence Stokes shifts (TDFS) for suitable charge-transfer excited states. While the solvent-dependent kinetics obtained in some aprotic media are consistent with the TDFS measurements, the barrier-crossing dynamics in several associated and/or highly polar liquids are indicative of much faster relaxation than inferred from TDFS. The possible nature, and implications, of these rapid modes are discussed. | | | |
| 20 DISTRIBUTION / AVAILABILITY OF ABSTRACT <input type="checkbox"/> UNCLASSIFIED/UNLIMITED <input checked="" type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS | | 21 ABSTRACT SECURITY CLASSIFICATION Unclassified | |
| 22a NAME OF RESPONSIBLE INDIVIDUAL | | 22b TELEPHONE (Include Area Code) | 22c OFFICE SYMBOL |

Keywords:

Solvent Relaxation in Thermal Electron-Transfer Reactions:
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| MS. EAS | <input type="checkbox"/> |
| Unpublished | <input type="checkbox"/> |
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| Institution | |
| Availability Status | |
| Dist. | Availability or special |
| A-1 | |

Submitted to Chemical Physics Letters.

ABSTRACT

The role of solvent dielectric relaxation on the barrier-crossing dynamics for outer-sphere electron transfer (ET), as evaluated from the solvent-dependent kinetics of metallocene self-exchange reactions, is compared with recent real-time measurements of polar solvation dynamics obtained from time-dependent fluorescence Stokes shifts (TDFS) for suitable charge-transfer excited states. While the solvent-dependent kinetics obtained in some aprotic media are consistent with the TDFS measurements, the barrier-crossing dynamics in several associated and/or highly polar liquids are indicative of much faster relaxation than inferred from TDFS. The possible nature, and implications, of these rapid modes are discussed.

Although the important role of the solvent medium in determining the free-energy barrier, ΔG^* , for electron-transfer processes has long been recognized,¹ its influence upon the barrier-crossing dynamics has only recently been treated theoretically,² and subsequently afforded detailed experimental scrutiny.^{3,4} By utilizing probe reactions having suitable characteristics (such as a small barrier contribution from intramolecular distortions), and by taking proper account of the variation in ΔG^* with the solvent, kinetic data for electron-exchange reactions can yield at least approximate information on the dependence of the barrier-crossing frequency, ν_n , upon the solvent properties.⁴ Comparison with the corresponding solvent-dependent frequencies predicted from conventional dielectric continuum treatments yields reasonable agreement in some cases,³ although some substantial deviations between the experimental and predicted frequencies have come to light.^{3d,4b,c}

Concurrent with (yet independent of) these activities, real-time measurements of the dynamics of dipolar solvation have been undertaken by utilizing time-dependent fluorescence Stokes shifts (TDFS) for chromophores forming suitable charge-transfer excited states.⁵⁻⁸ While the majority of these measurements have been restricted to relatively long timescales (> 10 ps) in some recent studies have examined solvent relaxation times down to ca. 0.2 ps.^{6a,c,7} Comparisons between the experimental TDFS relaxation times, τ_s , and the longitudinal times, τ_L , predicted from the dielectric continuum model indicate that typically $\tau_s \geq \tau_L$, although multiexponential decay behavior is commonly observed.⁶⁻⁸

Prompted in part by these experimental studies, increasing attention is being focused on the manner and extent to which solvent relaxation

attending charge transfer may differ from the conventional dielectric-continuum picture.^{6d,9} In particular, mechanisms accounting for multiexponential relaxation have been identified, including the expectation that $\tau > \tau_1$ for solvent molecules nearby the solute as a consequence of diminished dipole interactions.^{6d,9}

Given the current rapid evolution in both experimental and theoretical aspects of charge solvation dynamics, it is clearly of interest to compare these results and concepts with corresponding information on the dynamics of electron-transfer barrier crossing. In particular, there is a need to identify the components of the overall dielectric response having the most relevance to the barrier-crossing problem. Such a comparison is considered here, utilizing our recent data on the solvent-dependent kinetics for metallocene self-exchange reactions.^{4c} While necessarily preliminary, we believe that its significance is heightened by the emerging new perspectives of dynamical solvent effects in chemical reactivity.

Results and Discussion

Unlike TDFS measurements of dielectric solvent relaxation, which are extracted relatively directly from time-dependent Stokes shifts,¹⁰ the evaluation of such effects in the dynamics of barrier crossing for intermolecular electron transfer requires consideration of the influence of barrier energetics upon the observed rate constant, k_{ob} . A useful formalism for this purpose is expressed as^{11,12}

$$k_{ob} = K_p \kappa_{01} \nu_n \exp(-\Delta G^*/RT) \quad (1)$$

where K_p is the equilibrium constant for forming the appropriate

internuclear geometry, and κ_{01} is the electronic transmission coefficient.

We have recently employed this relation to extract solvent-dependent barrier-crossing frequencies, ν_n , from k_{ob} values obtained for metallocene self-exchange reactions using the proton nmr line-broadening technique.^{4c,13} These reactions, involving cobalticinium-cobaltocene, $Cp_2Co^{+/0}$ (Cp = cyclopentadienyl), its decamethyl derivative, $Cp'_2Co^{+/0}$ (Cp' = pentamethyl-cyclopentadienyl), and ferricinium-ferrocene, $Cp_2Fe^{+/0}$, have several virtues for this purpose, as detailed earlier.⁴ These include the presence of only small inner-shell (i.e. reactant intramolecular) barriers, small or negligible work-term effects upon K_p , and the stability and nonspecific solvation of the reactants in a variety of nonaqueous media.

The estimation of absolute ν_n values for such electron-exchange processes is hampered not only by uncertainties in K_p but, most critically, in the ΔG^* values. However, relative ν_n values in different solvents can be evaluated, at least approximately, since K_p should be roughly constant and there is good evidence* that the required solvent dependence of ΔG^* can be described for self-exchange reactions by the conventional dielectric continuum formula¹⁴

$$\Delta G_{os}^* = (e^2/4)(a^{-1} - R^{-1})(\epsilon_{op}^{-1} - \epsilon_s^{-1}) \quad (2)$$

where e is the electronic charge, a is the reactant radius, R is the internuclear distance (commonly presumed to equal $2a$), and ϵ_{op} and ϵ_s are the optical and static dielectric constants, respectively.

*This includes measurements of optical intervalence transition energies, E_{op} , in mixed-valence compounds, such as analogs of the metallocenes considered here,¹⁵ in which the solvent-dependent E_{op} values vary approximately in accordance with Eq (2).^{15,16}

The central issue here is the role of solvent dielectric relaxation in the barrier-crossing frequency. While the solvent sensitivity of ν_n implies that $\kappa_{e1} \approx 1$ (i.e. reaction adiabaticity is achieved),¹⁷ ν_n may be influenced by reactant vibrations. This contribution, however, is likely to be minor for the present metallocene systems since the inner-shell component of ΔG^* is relatively small, ca 10%.⁴ Under these circumstances, then, we can simply regard ν_n to be related to the effective relaxation time, τ_{eff} , by

$$\nu_n = \tau_{eff}^{-1} \quad (3)$$

The comparison between such solvent-dependent τ_{eff} values for electron-transfer barrier crossing and corresponding TDFS relaxation times, τ_s , forms the objective here.

At least for a Debye fluid (i.e. that having a single relaxation time, τ_D), dielectric continuum treatments of the barrier-crossing dynamics in terms of one-dimensional overdamped motion^{2a,b} lead to relations of the type^{4a,17}

$$\nu_n = K \tau_L^{-1} \quad (4)$$

where the longitudinal relaxation time τ_L is related to τ_D , obtained from dielectric loss spectra, by $\tau_L = (\epsilon_\infty/\epsilon_s)\tau_D$, with ϵ_∞ being the "infinite frequency" dielectric constant. Although the proportionality constant K in Eq (4) depends somewhat on ΔG^* as well as on the shape of the barrier top,^{2b} this dependence is relatively mild so that usually K is within ca twofold of unity for weak-overlap electron exchange.¹⁷ Under these circumstances, then, we expect that τ_{eff} can be equated approximately with

τ_L . A related treatment for solvents exhibiting multiple dielectric relaxation yields the conclusion that τ_{eff} is influenced disproportionately by the faster relaxation mode(s), so that $\tau_{eff} < \tau_{L1}$, where τ_{L1} is the often-predominant "slow" relaxation.^{2c} On the other hand, at least for Debye solvents we might anticipate that $\tau_{eff} > \tau_L$ as a result of short-range solvent contributions to τ_{eff} , as noted above.^{9a}

Given this situation, it is instructive to examine the solvent-dependent electron-transfer results in the light of the continuum predictions as a preface to comparison with corresponding TDFS data. Table I summarizes rate constants for self exchange, k_{ex} , for $Cp_2Co^{+/0}$, $Cp_2'Co^{+/0}$, and $Cp_2Fe^{+/0}$ in fifteen solvents, expressed as rate ratios with respect to those in the "reference solvent" dimethylsulfoxide, $k_{ex}/k_{ex}(ref)$. The data for the cobaltocene and ferrocene couples are extracted from refs. 4c and 18, respectively. Although the choice of reference solvent is somewhat arbitrary, dimethylsulfoxide was selected since it displays Debye-like dielectric loss behavior¹⁹ and TDFS relaxation kinetics.^{6a} Listed alongside are the corresponding τ_{eff} estimates for these probes in each solvent, again quoted as ratios to respect to the value in DMSO, $\tau_{eff}/\tau_{eff}(ref)$. The latter were obtained from the rate ratios by using [cf. Eq. (1)]:

$$[\tau_{eff}/\tau_{eff}(ref)]^{-1} = [k_{ex}/k_{ex}(ref)] \exp\{[\Delta G_{os}^* - \Delta G_{os}^*(ref)]/RT\} \quad (5)$$

where the ΔG_{os}^* estimates were obtained from Eq. (2) (see Table I footnotes). This procedure therefore assumes that K_p (and κ_{e1}) are solvent independent (vide supra). While the absolute k_{ex} values in each solvent are markedly different for the three probe reactions (apparently due to

electronic coupling effects on $K_p \kappa_{\bullet 1}$ ¹³), the rate and relaxation time ratios are largely similar in a given solvent.

Also listed in Table I are the corresponding longitudinal relaxation time ratios, $\tau_L/\tau_L(\text{ref})$, obtained from dielectric loss data. Comparison between the corresponding $\tau_{\bullet ff}/\tau_{\bullet ff}(\text{ref})$ and $\tau_L/\tau_L(\text{ref})$ values reveals that while these ratios are in reasonable agreement (within ca. twofold of each other) in a number of solvents, some substantial discrepancies are present. Most notably, the $\tau_{\bullet ff}$ values in methanol and ethanol are at least 50 fold smaller than expected from τ_L . This anomaly has been noted previously on the basis of related electrochemical exchange kinetics.^{3d,4b} Qualitatively similar discrepancies between the relative $\tau_{\bullet ff}$ and τ_L values are also seen in Table I for propylene carbonate and especially N-methylformamide (NMF).

The TDFS solvation dynamics of four of the solvents in Table I, acetonitrile, DMSO, nitrobenzene, and methanol, have been examined by Castner et al. for timescales down to ca. 0.5 ps using the fluorescence probe LDS-750.^{6a} The τ_s value in acetonitrile is about tenfold smaller than in DMSO [i.e. $\tau_s/\tau_s(\text{ref}) \approx 0.1$], in rough accordance with the corresponding τ_L ratio (Table I), even though τ_s is ca. 1.5-2 times τ_L .^{6a} This behavior is in good accordance with the corresponding $\tau_{\bullet ff}/\tau_{\bullet ff}(\text{ref})$ ratios in Table I. The solvation dynamics observed in nitrobenzene and methanol,^{6a} however, differ significantly from that expected from the corresponding $\tau_{\bullet ff}$ data in Table I. Biexponential relaxation behavior was obtained in nitrobenzene, with the predominant τ_s value being 4 fold smaller than τ_L . This yields $\tau_s/\tau_s(\text{ref}) \approx 0.5$ in this solvent, as compared with $\tau_{\bullet ff}/\tau_{\bullet ff}(\text{ref}) \approx 2$ for nitrobenzene and the dielectrically similar solvent benzonitrile (Table I). For methanol Castner et al. found that

$\tau_s/\tau_s(\text{ref}) \approx 1$ which stands in marked contrast to the corresponding relaxation times for barrier-crossing, $\tau_{\text{eff}}/\tau_{\text{eff}}(\text{ref}) \approx 0.05$ (Table I). Indeed, the τ_{eff} values are indicative of dielectric relaxation in methanol that is at least as rapid as in acetonitrile, whereas the τ_s value in the latter solvent is around tenfold shorter than in the latter.^{6a}

More striking differences between the barrier-crossing and real-time solvent relaxation behavior are exposed by examining some recent TDFS data obtained using Coumarin 153 as the fluorescence probe.^{6b} Although the relaxation timescale was restricted to $> \text{ca. } 30 \text{ ps}$ in these measurements, and multiexponential decay behavior was typically observed, average τ_s values were obtained in propylene carbonate (PC) and N-methylpropionamide (NMP) that are markedly (5-10 fold) longer than the corresponding τ_L values. These and other data are indicative of a correlation between τ_s/τ_L and the solvent dielectric constant, ϵ_s , since $\epsilon_s \approx 75\text{-}300$ in PC and NMP under the conditions employed.^{6b-d} This behavior is qualitatively in accordance with the MSA treatment of Wolynes,^{9a} which predicts that the short-range relaxation time, τ_G , is longer than τ_L to an extent increasing with ϵ_s .^{6b} A difficulty, however, is that the likely concomitant changes in ϵ_∞ and the solvent size can blur this prediction.

For comparison purposes, a plot of $\log(\tau_{\text{eff}}/\tau_L)$ versus $\log \epsilon_s$, where τ_{eff} and τ_L refer to the relaxation times relative to those in DMSO as listed in Table I, is shown in Fig. 1. The data for each solvent is numbered according to the scheme in Table I. In contrast to the $\log(\tau_s/\tau_L) - \log \epsilon_s$ behavior noted in ref. 6b, the $\log(\tau_{\text{eff}}/\tau_L)$ values in Fig. 1 are seen to decrease continuously (and roughly linearly) for solvents with progressively higher ϵ_s values. In particular, the solvents

having the highest dielectric constants, PC and NMF ($\epsilon_s = 65$ and 182, respectively), yield $(\tau_{eff}/\tau_L) \ll 1$. The only marked divergence is that also (τ_{eff}/τ_L) for methanol and ethanol, even though these solvents exhibit small or moderate ϵ_s values. [Although choosing "reference solvents" other than DMSO will alter these ratios, the effect is slight provided that simple aprotic media (e.g. acetonitrile) are selected.]

Taken together, then, these comparisons indicate that *qualitatively different* deviations from the dielectric continuum picture are observed for charge-transfer solvent relaxation in the barrier-crossing and TDFS cases. In particular, for solvents that exhibit substantial hydrogen bonding (methanol, ethanol, NMF) or are highly polar (PC), τ_{eff} values are obtained that are unexpectedly short on the basis of the available TDFS results as well as from the dielectric continuum predictions. The most likely explanation for these disparities is that the barrier-crossing dynamics are dominated in these cases by especially rapid relaxation modes that are of insufficient importance to the overall dielectric polarization spectrum and/or refer to timescales that are too short to be detected so far by the TDFS measurements. This line of argument is aided considerably by the likelihood, noted above, that τ_{eff} will be influenced disproportionately by such high-frequency components^{2c} such that $\tau_{eff} < \tau_L$.

The clearcut detection of such modes in dielectric loss spectra, however, is largely thwarted by the paucity of data at sufficiently high frequencies, together with interference from lower-frequency, yet predominant, relaxations.²⁰ Nonetheless, components having dielectric relaxation times, around 1 ps, much shorter than the major τ_D value have been identified for alcohols, including methanol and ethanol,²¹ and other

hydrogen-bonded solvents.²² Translational solvent motion may also provide an important relaxation pathway, at least in methanol.²³ Another candidate relaxation mode is associated with the cooperative rotations and/or librations within solvent cages,^{24,25} which are believed to be partly responsible for the difference between ϵ_{∞} and ϵ_{op} for polar fluids.²⁰ Since the importance of this mode apparently depends on the solvent dipole moment,²⁰ it may provide an explanation for the form of Fig. 1.

Irrespective of the detailed nature of these fast relaxations, it appears that the slower decay components observed in the TDFS experiments, especially in the more polar and self-associated media, may not contribute importantly (or even significantly) to barrier-crossing dynamics in electron transfer, and by inference in other reactions featuring charge transfer. Given the importance of faster components of the dielectric relaxation, it will be of great interest to attempt the examination of these modes directly in TDFS experiments. Although the TDFS time resolution has previously been largely inadequate for this purpose, the current rapid improvements in subpicosecond laser techniques promise to provide a wealth of such information, of central importance in elucidating dynamical solvent effects in chemical reactions.

Acknowledgments

We were aided significantly by helpful discussions and preprints from Ed Castner, Mark Maroncelli, Graham Fleming, Paul Barbara, and John Simon. This work is supported by the Office of Naval Research.

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TABLE I. Relative Solvent Dielectric Relaxation Times, τ_{eff} , as Inferred from Rates of Metallocene Self-Exchange Reactions at 25°C.

| Solvent ^a | $\Delta C_{\text{os}}^{*b}$ kcal mol ⁻¹ | $k_{\text{ex}}/k_{\text{ex}}(\text{ref})^c$ | | $\tau_{\text{eff}}/\tau_{\text{eff}}(\text{ref})^g$ | | $\tau_L/\tau_L(\text{ref})^h$ | | |
|--------------------------------------|---|---|--------------------------------|---|--------------------------------|-------------------------------|------|--------|
| | | $\text{Cp}_2\text{Co}^{+/o d}$ | $\text{Cp}_2\text{Co}^{+/o e}$ | $\text{Cp}_2\text{Co}^{+/o d}$ | $\text{Cp}_2\text{Co}^{+/o e}$ | | | |
| 1. DMSO | 4.8 | (1.9 x 10 ⁸) | (2.4 x 10 ⁷) | (1.6 x 10 ⁶) | | | | |
| 2. Acetonitrile | 5.75 | 2.3 | 1.6 | 3.3 | 0.10 | 0.13 | 0.06 | ~ 0.08 |
| 3. Acetone | 5.4 | 1.2 | 0.8 | 2.9 | 0.3 | 0.45 | 0.12 | 0.13 |
| 4. CH ₂ Cl ₂ | 4.2 | | 3.7 | 2.7 | | 0.75 | 1.0 | 0.17 |
| 5. (CH ₂ Cl) ₂ | 4.15 | | 2.6 | 2.7 | | 1.1 | 1.0 | 0.65 |
| 6. Pyridine | 4.0 | | 1.9 | | | 2.0 | | 0.5 |
| 7. DMF | 5.05 | 1.1 | 1.1 | | 0.6 | 0.6 | | 0.55 |
| 8. NMF | 5.3 | | 2.8 | | | 0.15 | | 1.5 |
| 9. PC | 5.25 | 1.5 | 1.2 | | 0.3 | 0.4 | | 1.1 |
| 10. Benzonitrile | 4.2 | 1.3 | 2.5 | | 2.1 | 1.1 | | 2.4 |
| 11. Nitrobenzene | 4.2 | | | 1.4 | | | 1.8 | 2.2 |
| 12. TMU | 4.75 | | 0.5 | | | 2.2 | | ~ 2.5 |
| 13. HMPA | 4.75 | 0.19 | 0.22 | | 5.3 | 4.5 | | 3.7 |
| 14. Methanol | 5.85 | | 3.0 | 3.8 | | 0.06 | 0.05 | 3.4 |
| 15. Ethanol | 5.45 | | 2.5 | | | 0.13 | | 9.2 |

Footnotes to Table I

^a DMSO - dimethylsulfoxide; CH_2Cl_2 - dichloromethane; $(\text{CH}_2\text{Cl})_2$ - 1,2-dichloroethane; DMF - N,N'-dimethylformamide; NMF - N-methylformamide; PC - propylene carbonate; TMU - tetramethylurea; HMPA - hexamethylphosphoramide.

^b Outer-shell (i.e. solvent) reorganization energy for self-exchange reactions in a given solvent, estimated from Eq. (2), with $a = 3.8 \text{ \AA}$, $R = 2a$, and using literature dielectric constant data (see ref. 4 for details).

^c Ratio of observed rate constants for self exchange of listed redox couple in given solvent to that in dimethylsulfoxide, obtained by proton nmr line broadening technique.^{4c,13,18} Ratios for $\text{Cp}'_2\text{Co}^{+/0}$ from ref. 4c, and for $\text{Cp}_2\text{Fe}^{+/0}$ from ref. 18. Quantities listed in parentheses are absolute values of k_{ex} ($\text{M}^{-1} \text{ s}^{-1}$) measured in DMSO. (For $\text{Cp}'_2\text{Co}^{+/0}$ and $\text{Cp}_2\text{Co}^{+/0}$, each solvent contained 0.1 M tetraethylammonium tetrafluoroborate.^{7c,13})

^d $\text{Cp}'_2\text{Co}^{+/0}$ - decamethylcobaltocenium-decamethylcobaltocene.

^e $\text{Cp}_2\text{Co}^{+/0}$ - cobaltocenium-cobaltocene.

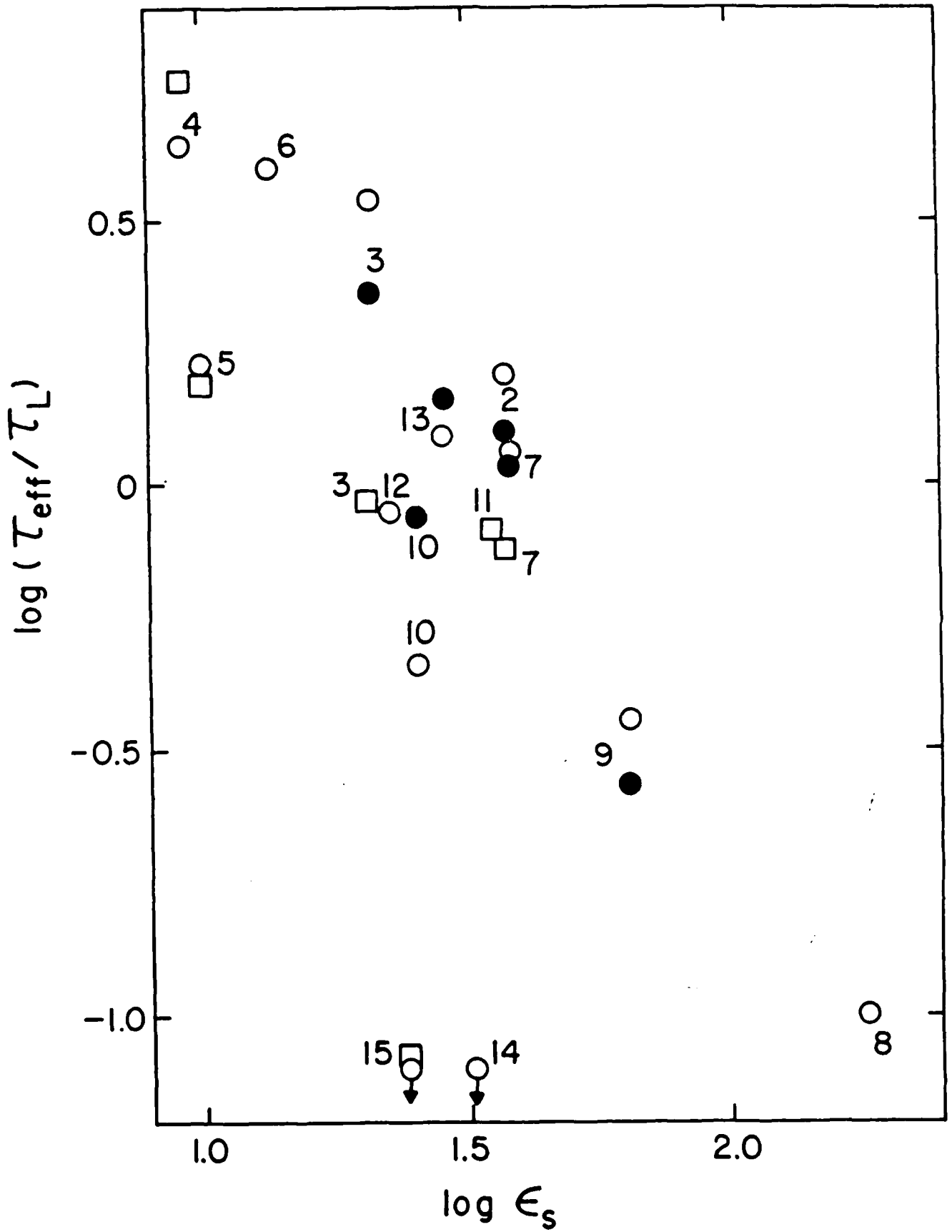
^f $\text{Cp}_2\text{Fe}^{+/0}$ - ferrocenium-ferrocene.

^g Ratio of effective relaxation time for barrier crossing in given solvent to that in the "reference solvent", dimethylsulfoxide. Obtained from corresponding $k_{\text{ex}}/k_{\text{ex}}(\text{ref})$ values and ΔG_{os}^* estimates using Eq. (5). (See text for details.)

^h Ratio of longitudinal relaxation time in given solvent to that in dimethylsulfoxide. Obtained from experimental Debye relaxation times, τ_D , by using $\tau_L = \tau_D (\epsilon_\infty/\epsilon_S)$ (see ref. 4 for details and literature sources).

Caption to Fig. 1

Logarithm of ratio of effective relaxation time for barrier crossing in metallocene self exchange reactions, τ_{eff} , to longitudinal relaxation time in a given solvent, τ_L , versus the logarithm of the static dielectric constant. Ratios taken with respect to values in dimethylsulfoxide; see text for calculational details. Key to reactions: filled circles, $\text{Cp}'_2\text{Co}^{+/0}$; open circles, $\text{Cp}_2\text{Co}^{+/0}$; open squares, $\text{Cp}_2\text{Fe}^{+/0}$. See Table I for key to solvent numbers and reactant symbols.



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