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(35) Paths B and H may occur concertedly without the intervention of the hypothetical vibrationally excited intermediate X. In solution, relaxation of such intermediates is generally regarded as occurring faster than chemical reaction. The state X is included to provide an overview of reaction pathways and because the role, if any, of such vibrationally excited intermediates in very complex molecules, such as cobaloximes, cannot be assessed at the present time. Similar considerations hold for paths D and E and the vibrationally excited intermediate XI.
(36) A detailed study of the kinetics and mechanism of the replacement of pyridine by tri-*n*-butylphosphine has been made and demonstrates conclusively that the mechanism is a pure dissociative process proceeding through the base-off complex: F. R. Jensen and R. C. Kiskis, *J. Am. Chem. Soc.*, preceding paper in this issue.
(37) Extinction coefficients for λ_{max} in the charge transfer region for several alkylcobaloximes with bases varying from very weakly to very strongly coordinating are given in ref 31. They vary only about a factor of 2 having 1.5×10^3 as about the maximum for the simple alkyl cobaloximes.
(38) Support for this line of reasoning comes from ref 31, where photolysis rate constants cleanly first-order in cobaloxime were obtained under conditions essentially identical with those reported in the present work.
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Solvent Effects in the Kinetics of Electron Transfer between *N*-*n*-Butyl-phthalimide Radical Ion and Its Parent Molecule

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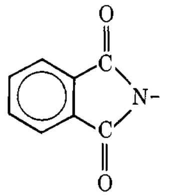
Received March 10, 1975

Abstract: The bimolecular rate constants, k_{ex}, of electron transfer between radical anions of *N*-*n*-butyl-phthalimide and its parent compound (BuPI) were determined in five solvents over temperatures ranging from −40 to +45°. The rate of exchange was derived by matching the experimental ESR spectra with those simulated by computer. The experimental and the computer-simulated spectra are extremely sensitive to minute variations in the coupling constants which therefore have to be determined with a high degree of accuracy.

Our previous studies[1,2] of *intra*molecular electron exchange between two aromatic end groups linked by molecular chains were extended recently to compounds having the structure

$$\text{PI-(CH}_2\text{)}_n\text{-PI or PI-(CH}_2\text{CH}_2\text{O)}_i\text{-CH}_2\text{CH}_2\text{-PI}$$

where PI denotes the phthalimide moiety



Evaluation of the results of that work, reported in the following paper,[3] calls for analysis of the ESR spectra of *N*-butylphthalimide (BuPI) radical anions in a variety of solvents and for determination of the bimolecular rate constants of exchange

$$\text{BuPI}\cdot^- + \text{BuPI} \overset{k_{ex}}{\rightleftarrows} \text{BuPI} + \text{BuPI}\cdot^-$$

measured in those solvents over a wide range of temperatures. Our findings are summarized in this paper.

Coupling Constants of Bu–PI·⁻

The ESR spectrum of BuPI·⁻ radical anions was reported by Hirayama[4] and that of the closely related ethyl derivative was studied by Nelsen[5] as well as by Hirayama.[4] Our results are listed in Table I. Solvents affect the values of the coupling constants only slightly; nevertheless, these small changes strongly modify the shape of the recorded spectrum as illustrated by Figure 1. For the same reason, the shape of the computer-simulated spectrum of BuPI·⁻ in acetonitrile deviates appreciably from the recorded one when Hirayama's coupling constants are adopted in the simulation. However, their slight alterations, shown in the last column of Table I, yield a simulated spectrum that fully resembles the experimental one. Therefore, it has been imperative to obtain highly accurate coupling constants to ensure the reliability of the results discussed in the following paper. The constants listed in Table I are reliable within ±0.05 G.

Kinetics of Exchange: BuPI·⁻ + BuPI → BuPI + BuPI·⁻

The bimolecular rate constants, k_{ex}, of this exchange reaction have been determined by the method outlined by Norris.[6] The BuPI·⁻ radical ions were dissolved in the chosen solvent together with the required amounts of the parent compound and their ESR spectra recorded at various temperatures. The recorded spectra were matched then with the computer-simulated ones.

The computer-drawn spectra were simulated for various lifetimes, τ of the radicals, using the coupling constants listed in Table I. The results were virtually identical whether the $1/T_2$ value fed into the computer was 30 or 60 mG, provided $1/\tau \geq 0.2$ G. For $1/\tau < 0.2$ G, it was necessary to assume $1/T_2 = 60$ mG in order to simulate the shape of the experimental spectrum observed in the absence of exchange. This is caused by the incapability of our spectrometer to resolve lines narrower than 60 mG. Consequently, the value $1/T_2 = 60$ mG was adopted in all our computations.

For the sake of illustration, the recorded spectra of the radicals dissolved in HMPA in the presence of 1.5×10^{-2} *M* of the phthalimide are shown in Figure 2 together with

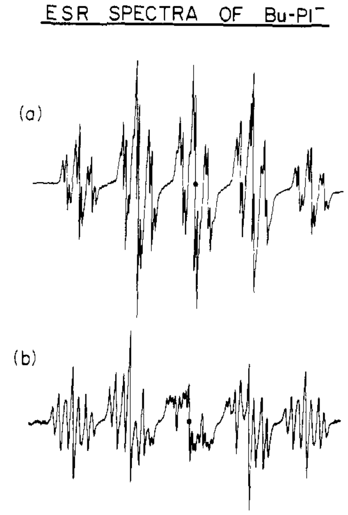
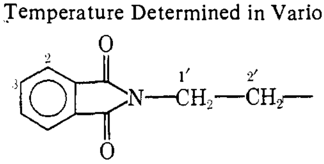


Figure 1. Experimental ESR spectra of BuPI·⁻ in HMPA (above) and in AN (below) at room temperature.

Table I. Coupling Constants of (*n*-Butyl)-*N*-phthalimide Radical Anions at Room Temperature Determined in Various Solvents[a]



	a, G					
Position[b]	In HMPA[c]	In DMF	In DMAc[c]	In DME[c]	In PN	In AN[d]
Nitrogen	2.47	2.42	2.45	2.40	2.40	2.45 (2.55)
2-Proton	0.13	0.205	0.19	0.185	0.205	0.23 (0.23)
3-Proton	2.34	2.39	2.44	2.45	2.40	2.325 (2.39)
1′-Proton	0.535	0.55	0.54	0.55	0.56	0.54 (0.57)

[a] Abbreviations: (HMPA) hexamethylphosphoric triamide, (DMF) *N,N*-dimethylformamide, (DMAc) *N,N*-dimethylacetamide, (DME) dimethoxyethane, (PN) propionitrile, (AN) acetonitrile. [b] The assignment of coupling constants to the ring protons taken from ref 4 and 5. [c] In this solvent, the coupling constants are insensitive to temperature variation. [d] The values in brackets are taken from ref 4.

the matched computer-simulated spectra. Thus, the rate of exchange was determined for each temperature. Using this approach, we determined the k_{ex} from the slopes of the lines giving $1/\tau$ as a function of [BuPI] for temperatures ranging from −15 to +45°. Such lines are shown in Figure 3 (1 G = 1.76×10^7 rad/sec). In a similar way, k_{ex} was determined in other solvents.

Experimental Section

Hexamethylphosphoric triamide (HMPA) and 1,2-dimethoxyethane (DME) were dried over potassium and $LiAlH_4$, respectively, and vacuum distilled into sealed containers. *N,N*-Dimethylformamide (DMF) and *N,N*-dimethylacetamide were kept for several days over KOH, fractionated, and then dried with CaH_2 in evacuated vessels. Acetonitrile (AN) and propionitrile (PN) were fractionated and then dried with CaH_2 in evacuated flasks. Each solvent was finally distilled on a high vacuum line into calibrated ampoules equipped with breakseals.

Solutions of BuPI·⁻ radical anions in HMPA were prepared by reducing the imide with potassium in DME and then replacing the ether by HMPA. Alternatively, the reduction was carried out electrochemically in HMPA. Identical ESR spectra were obtained from either preparation. Electrochemical reduction was used in the preparation of BuPI·⁻ in other solvents. The electrolytic cell consisted of two flat platinum electrodes separated by a fine glass filter and operated on 5-V potential. Tetrabutylammonium perchlorate in about 5×10^{-3} *M* concentration acted as the supporting electrolyte. The unit was evacuated and, after completion of the reduction, the solution from the cathodic compartment was transferred to an ESR tube attached to the cell. The ESR tube was then sealed off and inserted into the cavity of an ESR spectrometer. Thus prepared solutions were stable at room temperature for at least several days.

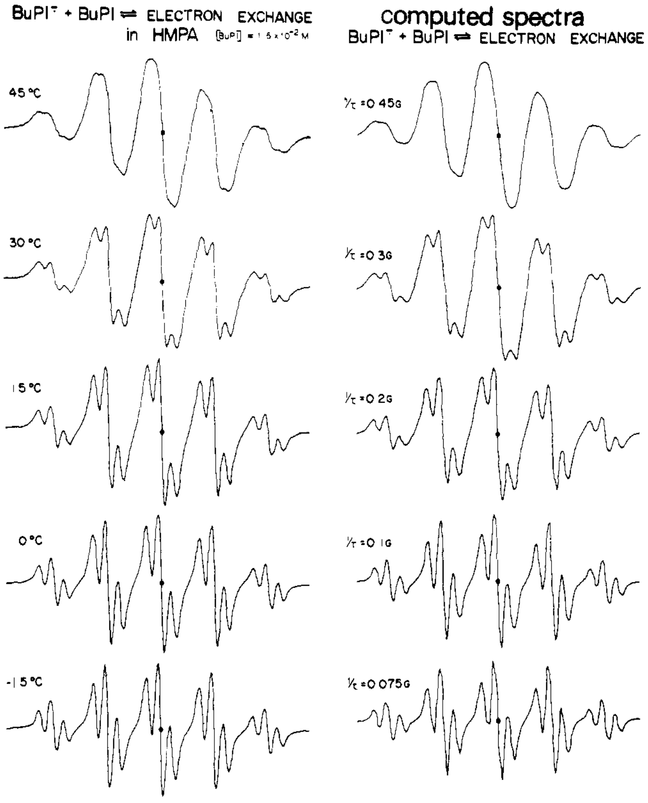


Figure 2. (Left) ESR spectra of BuPI·⁻ in HMPA recorded at various temperatures in the presence of 1.5×10^{-2} *M* of BuPI. (Right) The computer-simulated spectra.

The spectra were recorded on a Varian V-4504 spectrometer equipped with temperature controller calibrated by Cu-constantan thermocouple.

Results

The values of the bimolecular rate constants, k_{ex} are collected in Table II. The temperature dependence of k_{ex} is reliable for exchanges taking place in HMPA, DMAc, and in DME, because the pertinent coupling constants are virtually unaffected by the variation of temperature. However, the coupling constants characterizing the radical ions in DMF and in PN are slightly temperature dependent, and therefore we limited our kinetic studies to the region around ambient temperature. The large temperature dependence of *a*'s in acetonitrile prevented us from studying the exchange in this solvent.

The respective Arrhenius plots, shown in Figure 4, lead to the activation energies and frequency factors given at the bottom of Table II. These activation energies are higher, by about 1 kcal/mol, than the corresponding "activation energies" of the solvent's viscosity, the DME system being exceptional. The activation energy measured in that solvent exceeds the "activation energy" of viscosity of that ether by ~1.6 kcal/mol.

The rates of exchange are too slow for a diffusion-controlled reaction, although they might approach the diffusion limit in the highly viscous HMPA. It is striking how closely similar are the k_{ex} in HMPA, DMF, DMAc, and PN (see, e.g., the data pertaining to 20°) in spite of the large varia-

Table II. Electron Exchange, $BuPI\cdot^- + BuPI \overset{k_{ex}}{\rightleftarrows} BuPI + BuPI\cdot^{-a}$

	HMPA		DMF		DMAc		DME		PN	
T, °C	$k_{ex} \times 10^{-8}$, M^{-1} sec^{-1}	η (mp)	$k_{ex} \times 10^{-8}$, M^{-1} sec^{-1}	η (mp)	$k_{ex} \times 10^{-8}$, M^{-1} sec^{-1}	η (mp)	$k_{ex} \times 10^{-8}$, M^{-1} sec^{-1}	η (mp)	$k_{ex} \times 10^{-8}$, M^{-1} sec^{-1}	η (mp)
45	6.6	22.2								
40			3.9	4.92	4.3	7.29	2.9	3.86	5.3	3.53
30	4.2	30.3								
20	3.4 (interpol)		2.6	6.37	3.0	9.76	1.8	4.77	3.9	4.23
15	2.7	42.3								
0	1.8	62.4	1.8	8.89	1.7	13.7	1.2	6.10	2.8	5.35
−15	1.0									
−20				12.3	0.94	20.8	0.72	7.80	2.0	6.92
−40				19.0			0.40	11.3		9.81
E_{ex}, kcal/mol:	5.2		3.4		4.0		3.6		2.9	
A_{ex}, M^{-1} sec^{-1}:	2.4×10^{12}		8.5×10^{10}		2.5×10^{11}		8.6×10^{10}		6.1×10^{10}	
$-E_\eta$, kcal/mol:		3.9		2.4		2.8		1.95		1.85

[a] See Table I for solvent abbreviations.

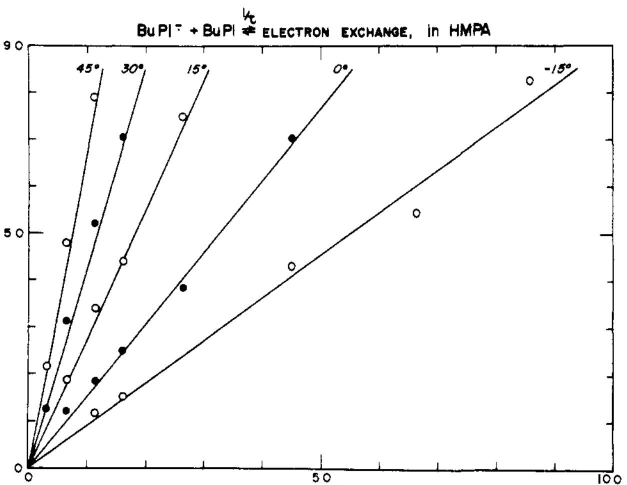


Figure 3. Plots of $1/\tau$ vs. [BuPI] for the exchange taking place in HMPA at various temperatures.

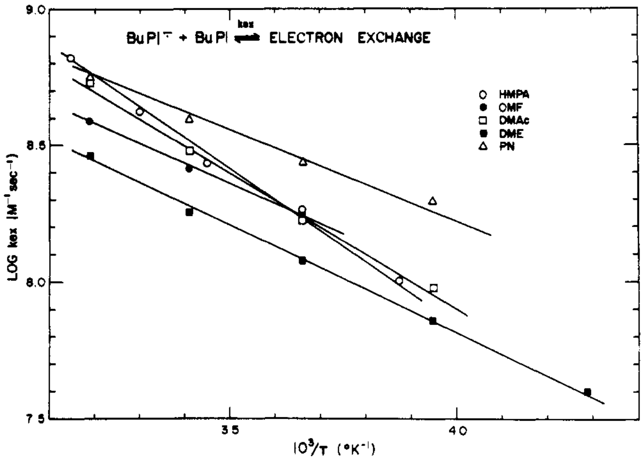


Figure 4. Arrhenius plots of log k_{ex} vs. $1/T$ for HMPA, DMF, DMAc, PN, and DME.

tions in the viscosities of these solvents. The lower value k_{ex} in DME probably reflects the ion pairing which takes place in this ether, while $BuPI\cdot^-$ ions probably remain free in the remaining solvents. The effect of ion pairing was noted in DMF, and probably it might be seen also in DMAc and PN if the concentration of the supporting electrolyte (Bu_4N^+,ClO_4^-) were increased from 5×10^{-3} to about 0.1 M.

Although it may be questioned whether the variations of activation energies given in Table II are significant or whether they reflect the experimental uncertainties, the higher value of E_{ex} in HMPA seems genuine. The relatively high values of E_{ex} imply that the ions are surrounded by weakly organized solvent molecules which become disorganized (desolvation) in the transition state of the transfer. This effect accounted for by Marcus' theory[7] is reflected in the relatively high frequency factor of the order 10^{11} M^{-1} sec^{-1}, whereas the usual frequency factor of 10^8–10^9 M^{-1} sec^{-1} is expected for a bimolecular reaction in the absence of solvent reorganization.

Final Conclusions

The bimolecular rate constants, k_{ex}, of the electron transfer

$$BuPI\cdot^- + BuPI \rightleftarrows BuPI + BuPI\cdot^-$$

are virtually independent of the nature of the solvent for HMPA, DMF, DMAc, and PN and amount to about 3×10^8 M^{-1} sec^{-1} at 20°. The reaction is slower in DME, presumably due to ion pairing. The transfer involves an activation energy of about 3.5 kcal/mol corresponding to an A_{ex} factor of about 10^{11} M^{-1} sec^{-1}. The exchange is slower than a diffusion-controlled reaction, and the partial desolvation of the anions in the transition state accounts for the relative slowness of that process. This "Marcus" effect is magnified in the polar butylphthalimide system when compared with the nonpolar butylnaphthalene and is responsible for $k_{ex}(N)/k_{ex}(PI) \sim 1.5$–$2$.

Acknowledgment. The financial support of this study by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by the National Science Foundation is gratefully acknowledged.

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