of us (J. S.) acknowledges a helpful discussion with Professor G. S Hammond.

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Direct Distinction between Ions and Ion Pairs in Electron-Transfer Reactions by Means of Electron Spin Resonance[1]

Sir:

Electron spin resonance (esr) has been shown to be uniquely suitable for measuring the rates of fast electron-transfer reactions between radical ions and neutral molecules in solution.[2] Depending on the nature of the solvents and the counterions, these radicals may exist as free ions, ion pairs,[3] or a mixture of both. Accordingly, electron-transfer reactions in the case of aromatic anion radicals can be represented by

$$R + R^- \rightleftharpoons R^- + R \quad (1)$$

$$R + M^+R^- \rightleftharpoons M^+R^- + R \quad (2)$$

where R is the neutral molecule, R^- the anion radical, and M^+ the alkali metal ion. In general it has not been possible to distinguish between reactions 1 and 2 since measurement of their individual rates requires the observation of distinctly different esr spectra for the two species. Except when M has an appreciable magnetic moment, *e.g.*, sodium, most of the ion-paired radicals show esr spectra which have unresolved metal splittings. The only measurements of rates which distinguish ions and ion pairs are those reported by Zandstra and Weissman for the naphthalene–naphthalenide system in tetrahydrofuran (THF) and similar solvents using sodium as the reducing agent.[4] The large sodium splittings and the detectable concentrations of both the free and ion-paired species enabled the observation of two overlapping esr spectra over a wide range of temperatures.

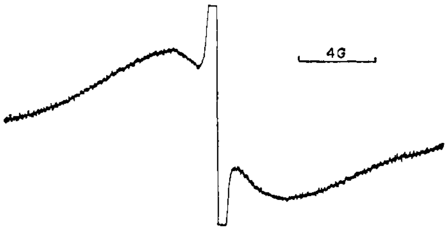

Figure 1. Esr first derivative spectrum obtained when naphthalene (1.4 *M*) was reduced with potassium in tetrahydrofuran. The clipped center peak indicates an off-scale reading.

We have been able to distinguish the free ion from the ion pair in certain cases and to separately measure the rates of their oxidation–reduction reactions by making use of the hitherto unexploited "fast exchange limit."[5] In this regime the entire spectrum for each species collapses to a single line of Lorentzian shape or possibly a set of equally spaced lines for atom transfers,[6] and the equation of Piette and Anderson can conveniently be used to determine the second-order rate constant for the exchange reaction.[7] When rewritten for this situation their equation becomes $k = 2.04 \times 10^7 \nabla/\Delta H[\mathrm{R}]$, where ∇ is the second moment (in gauss²) of the spectrum of the species of interest in the absence of exchange, ΔH is the line width[8] (in gauss) corrected for modulation, natural line width, etc., and [R] is the concentration (in moles/liter) of the neutral species. Of course, the measurement of more than one rate in a single experiment requires that the rates be well separated. A typical experimental curve is shown in Figure 1 to illustrate the separability of the species in our study.

By the above procedure rate constants have been measured for naphthalene in reactions 1 and 2 using THF and 1,2-dimethoxyethane (DME) as solvents and potassium and sodium as reducing agents. A summary of the results is given in Table I along with rate constants measured by Weissman and his co-workers for comparison. In the Na–DME system at high naphthalene concentrations, only one line was observed from −30 to +40°. When potassium was used as the reducing agent in DME, a single line was also observed; however, in THF two lines of appreciably different widths were found (see Figure 1). A second broad line was also observed in the K–DME system after the addition of potassium chloride. Finally, for the Na–THF combination we obtained a single line superimposed on a broad uncollapsed spectrum. As expected the strongly collapsed lines were always rigorously Lorentzian, thus confirming the fast exchange limit. The greatest errors

Table I. Rate Constants for Naphthalene–Naphthalenide Systems at 23°

Metal ion	Solvent	Species	Fast exchange limit, k, $M^{-1}\,\mathrm{sec}^{-1}$	Previous work,[a] k, $M^{-1}\,\mathrm{sec}^{-1}$
Na	DME	Ion	$(1.6 \pm 0.2) \times 10^9$	$(1 + 3 - 0.7) \times 10^9$
Na	THF	Ion[b]	$(2 \pm 1.5) \times 10^9$	$(8 \pm 4) \times 10^7$
		Ion pair	$<3 \times 10^7$	$(1.8 \pm 0.6) \times 10^7$
K	DME	Ion	$(2.2 \pm 0.4) \times 10^9$	
		Ion pair[c]	$(1.0 \pm 0.5) \times 10^8$	$(7.6 \pm 3) \times 10^7$
K	THF	Ion	$(3.0 \pm 0.5) \times 10^9$	
		Ion pair	$(6 \pm 2) \times 10^7$	$(5.7 \pm 1) \times 10^7$

[a] Obtained from ref 2 or calculated from the data in ref 4. [b] This measurement was hampered at the fast exchange limit by the presence of an uncollapsed background. [c] At the fast exchange limit this rate was measured in the presence of a 5 m*M* concentration of KCl.

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[1] This work was supported in part by grants from the Public Health Service (GM-12504) and the National Science Foundation (GP-4952).

[2] R. L. Ward and S. I. Weissman, *J. Am. Chem. Soc.*, **79**, 2068 (1957).

[3] There is good evidence that, in fact, a rapid equilibrium exists between two types of ion pairs and that the measured properties in esr (splitting constants, electron-transfer rates, etc.) depend on the equilibrium constant: N. Hirota and R. Kreilick, *J. Am. Chem. Soc.*, **88**, 614 (1966); T. E. Hogen-Esch and J. Smid, *ibid.*, **87**, 667 (1965).

[4] P. J. Zandstra and S. I. Weissman, *ibid.*, **84**, 4408 (1962).

[5] No quantitative rate measurements have been reported at this limit; however, crude estimates have been based on collapsed spectra; see, for example, J. W. Eastman, G. M. Androes, and M. Calvin, *Nature*, **193**, 1067 (1962).

[6] F. C. Adam and S. I. Weissman, *J. Am. Chem. Soc.*, **80**, 1518 (1958).

[7] L. H. Piette and W. A. Anderson, *J. Chem. Phys.*, 30, 899 (1959), 23.

[8] Here the line width is taken to mean the separation between the extrema in a first derivative spectrum.

were incurred in measuring broad weak signals and in those cases where collapsed lines were superimposed on uncollapsed spectra.

In all cases we have assigned the faster rate to the free ions on the basis of the following evidence. (1) The larger rate constants have essentially the same value and, furthermore, these reactions all have low activation energies ($\lesssim$5 kcal/mole). This is not consistent with the formation of different ion pairs. (2) The smaller rate constants all agree with Weissman's data. Conductance studies of aromatic anion radicals show that except in Na–DME all of the combinations of cation and solvents favor the formation of ion pairs at room temperature.[9] Thus in the slow exchange limit the measured rates must apply to reaction 2. The free ions show up so prominently in the collapsed spectra because of their narrow lines. This does not exhaust our arguments but should suffice.

The major discrepancy in Table I arises with the dissociated ion in the Na–THF system. We are not sure of the reason for this difference, but would like to point out that unwanted line width contributions are much more likely to introduce errors when one is working at the slow exchange limit. Our estimates of the rate constants for the ion pairs are in agreement with previous work but are not as accurate since the spectra could not be collapsed with reasonable naphthalene concentrations. Unfortunately, esr measurements give only a limited amount of information about the total system. We plan to supplement this work by means of a pulsed nmr study of ^{23}Na relaxation and, in particular, to determine the rate of dissociation of the ion pair.

In addition to providing access to previously concealed rate processes the technique described here shows considerable promise for complex systems since the esr spectra do not have to be either well resolved or analyzed. Our experiments on stilbene and other systems show that experimental second moments can easily be obtained which fall within 10% of those calculated from stick spectra. Solubility may present a problem, but if necessary it can be partially circumvented by deuterating the radicals to decrease the exchange rate required to collapse their spectra. We plan to make a more detailed report of our work at a later time.

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(9) K. H. J. Buschow, J. Dieleman, and G. J. Hoijtink, *J. Chem. Phys.*, **42**, 1993 (1965).

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Reactions of Phosphorus Trioxide with Some Compounds of the Group III Elements

Sir:

Phosphorus trioxide (P_4O_6) is expected[1] to donate lone-pair electrons to Lewis acids to give addition complexes without disruption of the P_4O_6 birdcage structure. On the other hand, exchange of parts between P_4O_6 and, for example, tricoordinated boron compounds might also be possible. Both situations have actually been observed.

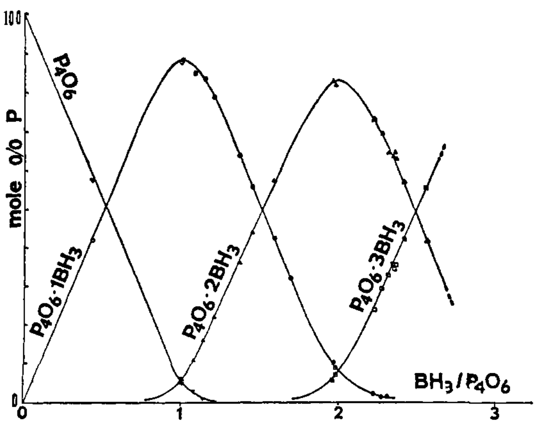

Figure 1. Distribution of species at equilibrium in the system P_4O_6 *vs.* B_2H_6 in chloroform solution at 25°. The open symbols refer to samples prepared by bubbling B_2H_6 through a chloroform solution of P_4O_6 and the half-shaded symbols to samples obtained by addition of P_4O_6 to a previously equilibrated sample or by admixing two such samples. The full-shaded symbols refer to samples obtained from $P_4O_6 \cdot 3BH_3$ crystals.

When diborane is slowly bubbled through a solution of P_4O_6 in dry chloroform at 25°, a reaction takes place which has been followed quantitatively by P^{31} nmr. Successive nmr spectra show a sequential reaction similar to that already observed between P_4O_6 with $Ni(CO)_4$.[1] The observed coupling constant and chemical shifts correspond to successive coordination of one, two, and three BH_3 groups around the P_4O_6. The P^{31} and H^1 nmr data for the individual species are presented in Table I.

Table I. Nmr Data for Phosphorus Trioxide–Borane Complexes[a]

	From P^{31} spectra			From H^1 spectra		
	$\delta_{\text{coord P}}$	$\delta_{\text{uncoord P}}$	$J_{\text{P-O-P}}$[b]	δ_{H}	$J_{\text{B-H}}$	$J_{\text{P-B-H}}$
$P_4O_6 \cdot BH_3$	−90.4	−118.2	27.5	−0.7	102	18
$P_4O_6 \cdot 2BH_3$	−98.7	−119.2	24.7	−0.65	∼100	
$P_4O_6 \cdot 3BH_3$	−103.6	−114.6	21			

[a] P^{31} spectra in *n*-hexane and H^1 spectra in $CHCl_3$. P^{31} chemical shifts, δ in ppm, are referenced to 85% H_3PO_4 but were measured with respect to P_4O_6 at −113 ppm. Proton chemical shifts, δ in ppm, are referenced to tetramethylsilane. Coupling constants *J*, are in cps. [b] $J_{\text{P-O-P}}$ represents the coupling constants between coordinated and uncoordinated phosphorus atoms.

The rate of incorporation of diborane at 1 atm pressure in the P_4O_6 solution is approximately constant until it stops at a ratio of total uncoordinated P to total P of *ca.* 1:3. The product then consists of an equilibrium mixture of *ca.* 64% $P_4O_6 \cdot 2BH_3$ and 36% $P_4O_6 \cdot 3BH_3$.

Well-formed crystals of the $P_4O_6 \cdot 3BH_3$ complex are observed to form when concentrated chloroform solutions corresponding to the maximum possible incorporation of diborane under 1 atm are cooled by Dry Ice. The crystals of $P_4O_6 \cdot 3BH_3$ are so unstable that we have been unable to dry them. When redissolved in chloroform, they decompose in a few minutes with evolution of B_2H_6 to give the above equilibrium mixture.

The reaction is seen to follow the same path when diborane is allowed to react with P_4O_6 in the absence of a solvent, but the $P_4O_6 \cdot 2BH_3$ complex then precipitates and the coordination of further BH_3 groups is thus prevented. This compound has been recrystallized as

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(1) J. Riess and J. R. Van Wazer, *J. Am. Chem. Soc.*, **87**, 5506 (1965).