the -C*H*D- resonance, whose triplet fine structure due to H,D coupling dissappears progressively. Line-shape analysis[1,17] gives T_q^D for various values of α.[15] Similar results are obtained for the [TNB, MF] and the [TNB, MPh] systems. Treatment of the data as described above leads to the values listed in Table I. The figure shows the experimental $T_q^D = f(\alpha)$ points and the corresponding best fitted theoretical curve for the [TNB, F] system.

Several conclusions may be drawn from these results (see Table I). (1) The rate of reorientation of the complexed D molecules, k_c, is much slower than that of the free molecules, k_f. Thus the complex behaves as a specific AD entity which undergoes reorientation as a single, discrete unit.[19] Using the Debye relation $\tau = 4\pi\eta a^3/3kT$ (with τ = rotational correlation time, a = radius of the rotating unit, and η = viscosity of the solution),[20] one finds that the "radius" of the [TNB, F] complex is *ca.* 1.8 times larger than that of the free F molecule. This result agrees with the fact that the TNB and F molecules are of comparable average "size" and that the distance between the TNB and F components in the complex should be of the order of 3.5 Å as in the [TNB, naphthalene] complex for instance.[21]

(2) The rate processes occurring in the present EDA systems are very fast (*ca.* 10/nanosecond (nsec) = 10^{10} sec^{-1}). The analysis of nuclear relaxation data (in particular of the quadrupolar type) may thus be a powerful method for studying extremely fast reactions (see also ref 14 and 19).

(3) The rate of dissociation, k_d, of the AD complex is comparable to its rate of reorientation, k_c, and is much slower than the rate of reorientation of free D molecules (k_f). In other words, the lifetime of the complex (k_d^{-1}) is longer than the correlation time for rotational motion of the free D molecules (k_f^{-1}) but is comparable to the correlation time of the complex (k_c^{-1}). The complex may be considered as being of the "collision complex" type ("contact charge-transfer" complexes of Mulliken and Orgel[22]).

(4) The correlation time of the -CH$_2$D group in MF is not affected by complex formation as may be expected from the rapid rate of internal rotation about the C-CH$_2$D bond which effectively decouples the motion of the -CH$_2$D group from the overall molecular reorientation.[1]

The present studies are being extended to other systems, especially to some more stable complexes, in order to arrive at a precise description of the molecular dynamics of complex formation. The application to ion-pair formation and to biological systems[23] (molecular dynamics of enzyme-substrate, drug-receptor model interactions) is also in progress.

(19) J. E. Anderson, *J. Chem. Phys.*, **51**, 3578 (1969).

(20) The Debye relation applies for spherical units undergoing isotropic reorientation. This is a gross approximation in the present case but allows, nevertheless, qualitative comparisons to be made.

(21) S. C. Wallwork, *J. Chem. Soc.*, 494 (1961).

(22) R. S. Mulliken and L. W. Orgel, *J. Amer. Chem. Soc.*, **79**, 4839 (1957).

(23) J. P. Behr, H. Goldwhite, and J. M. Lehn, unpublished results.

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Solvation Studies of Sodium and Lithium Ions by Sodium-23 and Lithium-7 Nuclear Magnetic Resonance

Sir:

In connection with a detailed study of ionic solvation carried out in this laboratory, it was decided to investigate the nuclear magnetic resonances of alkali metal ions in various solvents. This communication reports the results obtained with ^{23}Na nmr as well as some preliminary results observed with ^{7}Li nmr. Literature search indicated that such studies have been rather sparse, especially in nonaqueous solvents. The most detailed study found was that of Bloor and Kidd,[1] who measured the influence of solvents on the chemical shifts of ^{23}Na with respect to aqueous solutions. However, only sodium iodide was used as solute, and it was of interest to us to extend the studies to other sodium salts in order to observe possible influence of the anion on solvation.

A Varian DA-60 in wide-line configuration was modified to allow the recorder sweep potentiometer to sweep the magnet power supply for the ^{23}Na investigations at 15.9 MHz. Natural line widths for the ^{23}Na resonances are such that the use of 15-mm nonspinning samples did not significantly degrade our results. Shifts were calibrated using the side-band technique with a saturated solution of sodium chloride in water as the standard.

For the ^{7}Li investigations, the DA-60 was run in its normal locked configuration at 24.29 MHz. A saturated aqueous solution of lithium chloride was used as a standard.

Four sodium salts were thus far investigated, tetraphenylborate, perchlorate, iodide, and thiocyanate. It was immediately obvious that the nature of the anion plays a very important role in the resulting chemical shift. Confirming the results of Bloor and Kidd, the chemical shifts for sodium iodide solutions were concentration dependent. Likewise, the magnitudes of the chemical shifts and their solvent dependence were, in general, in good agreement with the previous results.[1] Chemical shifts for sodium thiocyanate were also concentration dependent, although to a lesser extent than those for the iodide.

A very different behavior, however, was found for the tetraphenylborate and the perchlorate. For example, the ^{23}Na resonance of the tetraphenylborate solutions in tetrahydrofuran, ethyl acetate, acetone, acetonitrile, and methanol did not show any concentration dependence in the 0.5–0.1 *M* concentration range. Only in nitromethane solutions was there a slight ($\sim$10 Hz) shift downfield with dilution. Corresponding solutions of sodium iodide were much more concentration dependent, with downfield shifts of $\geq$30 Hz for the same dilution. Likewise, the solvent dependence of the chemical shift (with reference to aqueous solutions) is quite different for the two salts, as seen from the data in Table I.

It seems reasonable to ascribe this difference in behavior of the four salts to the formation of ion pairs in the case of the iodide and, to some extent, of the thiocyanate. Thus, for the tetraphenylborate and the perchlorate the changes in the chemical shift of the cation are due only to changes in the shielding brought

(1) E. G. Bloor and R. G. Kidd, *Can. J. Chem.*, **46**, 3425 (1968).

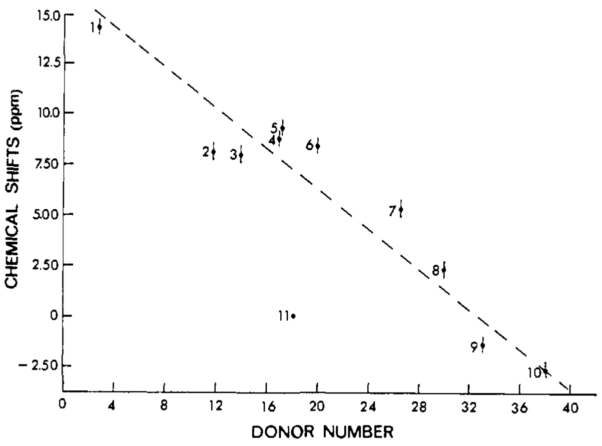

Figure 1. Plot of ^{23}Na chemical shifts *vs.* donor number of the solvents (1) nitromethane, (2) benzonitrile, (3) acetonitrile, (4) acetone, (5) ethyl acetate, (6) tetrahydrofuran, (7) dimethylformamide, (8) dimethyl sulfoxide, (9) pyridine, (10) hexamethylphosphoramide, (11) water.

about by the formation of the inner solvation shell. In such cases it would be expected that the chemical shifts would be related to the solvating abilities of the respective solvents. An empirical approach to the evaluation of the complexing (or donor) ability of the solvents is provided by Gutmann's "donor numbers."[2] The latter are simply the enthalpies (in kcal/mol) of complex formation between the given solvent and antimony pentachloride in 1,2-dichloroethane solutions. As shown by Gutmann, the donor numbers can be quite useful in predicting the behavior of nonaqueous systems. It was reasonable to expect, therefore, that there might be a relationship between the donor numbers and the relative chemical shifts for the solvated sodium ions. A plot of chemical shift *vs.* donor numbers (Figure 1) shows that this is indeed the case. The only discrepancy appears to be water, which, according to our data, should have a donor number of ~33 instead of 18 as given by Gutmann. The linearity of the plot shows that the relative chemical shifts of ^{23}Na yield useful information on the solvating abilities of the solvents at least *vis à vis* the sodium ion.

Table I. Chemical Shifts of Sodium-23 Resonance in Different Solvents[a]

Solvent	$NaPh_4B$, Hz	NaI, Hz
Hexamethylphosphoramide	−41	−40.6
Pyridine	−20	−60.0
Water	0	0
Dimethyl sulfoxide	+37	
Methanol	+72	
Dimethylformamide	+83	+67
Acetonitrile	+127	+76
Tetrahydrofuran	+124	−100
Acetone	+136	+55
Ethylacetate	+147	
Nitromethane	+256	

[a] 0.5 *M* solutions.

A preliminary experiment was performed on the complexation of the sodium ion with the crown compound dicyclohexyl-18-crown-6,[3] which is known to form strong complexes with the alkali metal ions.[4] Equimolar amounts of the crown compound and of sodium tetraphenylborate were dissolved in nitromethane, and the search was made for the ^{23}Na resonance. However, no evidence for this resonance was obtained. Increasing amounts of sodium tetraphenylborate were added to the solution and a *very broad* peak appeared with a chemical shift equal to that of the tetraphenylborate in pure nitromethane. It is evident that the strong interaction between the crown compound and Na^+ ion broadens the resonance to such an extent that it is no longer visible under our experimental conditions.

Preliminary results were also obtained with ^{7}Li nuclear magnetic resonance. Only lithium perchlorate was used thus far. The results, however, do not indicate the same correlation with the donor number as for ^{23}Na chemical shifts. A possible explanation for this difference in behavior may be the fact that in the case of ^{23}Na the paramagnetic shielding term σ_p is ~30 times larger than the diamagnetic term σ_d, and thus the former dominates the chemical shifts.[1] In the case of ^{7}Li, the values of the two terms are much closer, which may account for the variation in the chemical shifts. In general, our results agree with those of Akitt and Downs.[5]

It is seen from the above results that the use of nmr spectroscopy of the alkali nuclei makes a very important contribution to the elucidation of the structure of electrolyte solutions. This work is being continued.

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(2) V. Gutmann, "Coordination Chemistry in Nonaqueous Solutions," Springer-Verlag, Vienna, 1968, and references therein.

(3) C. J. Pedersen, *J. Amer. Chem. Soc.*, **89**, 7017 (1967).

(4) C. J. Pedersen, *ibid.*, **92**, 386 (1970).

(5) J. W. Akitt and A. J. Downs, "Alkali Metals Symposium," The Chemical Society, London, 1967, p 199.

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The Dynamic Stereochemistry of Some π-Allylpalladium Compounds

Sir:

Isomerization reactions of π-allylpalladium complexes have been the subject of several recent mechanistic investigations.[1,2] We wish to present evidence which confirms the most recent mechanistic proposals and comment on the effect of substituents on the magnitude of the energy barriers.

The ambient temperature spectrum of di-μ-chloro-bis(*trihapto*(*syn*-1-isopropylallyl))dipalladium(II)[3] (**1**) is summarized in Table I. The diastereotopic methyl

(1) J. W. Faller and M. E. Thomsen, *J. Amer. Chem. Soc.*, **91**, 6871 (1969).

(2) P. W. N. M. van Leeuwen and A. P. Praat, *Chem. Commun.*, 365 (1970).

(3) Using the nomenclature suggested by F. A. Cotton, *J. Amer. Chem. Soc.*, **90**, 6230 (1968). An alternative name is di-μ-chloro-bis-(*syn*-4-methylpent-1(3)-enyl)dipalladium(II).