

H_2SO_4 (or in FSO_3H) is similar to those reported previously.⁴⁻⁹ However, it should be noted that the absorption spectrum of ion **1**, measured at -60° in $\text{FSO}_3\text{H}-\text{SbF}_5$ (9:1 mole:mole)-ethanol solution,⁸ differs significantly from that obtained by us at room temperature in $\text{FSO}_3\text{H}-\text{SbF}_5$ (1:1 mole:mole) solution (without ethanol).

The present observations of triphenylcarbinol (**2**) in 20% oleum and in $\text{FSO}_3\text{H}-\text{SbF}_5$ (1:1 mole:mole) solution may indicate the formation of (i) sulfonation (fluorosulfonation) products, (ii) a solvent-separated ion pair ($\text{Ph}_3\text{C}^+\text{Y}^-$, or (iii) an associated ion pair ($\text{Ph}_3\text{C}^+\text{Y}^-$).¹² The formation of sulfonation products was ruled out because on quenching with water-ice, all the solutions gave a quantitative yield of starting material **2** (see also subsequent discussion). It is unlikely that solvent-separated ion pairs are formed in neat $\text{FSO}_3\text{H}-\text{SbF}_5$ (1:1 mole:mole) because a previous nmr study has shown that such species are not found under similar experimental conditions.¹³ We thus favor the formation of associated ion pairs ($\text{Ph}_3\text{C}^+\text{Y}^-$) in both 20% oleum and in $\text{FSO}_3\text{H}-\text{SbF}_5$ (1:1 mole:mole) solutions and cannot rule out the formation of such species in 100% H_2SO_4 and in FSO_3H .

In addition, we have studied (Table I) the absorption and MCD spectra of ion **1** in mixed superacid systems (1:1 v:v). The separation of the two absorption bands of ion **1** in 100% H_2SO_4 + 20% oleum and in 100% H_2SO_4 + $\text{FSO}_3\text{H}-\text{SbF}_5$ (1:1 mole:mole) solutions, prepared either by treating **2** with the superacid mixtures or by adding 20% oleum or $\text{FSO}_3\text{H}-\text{SbF}_5$ (1:1 mole:mole) solution to ion **1** in 100% H_2SO_4 was small. The spectra were similar to those observed in 100% H_2SO_4 and in FSO_3H where bands I and II were observed. When these solutions were warmed to 60° for 10 min, the separation of the two bands increased and the spectra were similar to those observed in 20% oleum and in $\text{FSO}_3\text{H}-\text{SbF}_5$ (1:1 mole:mole) solutions. On the other hand, when an equal volume of 100% H_2SO_4 was added to ion **1** in 20% oleum or $\text{FSO}_3\text{H}-\text{SbF}_5$ (1:1 mole:mole) solution and held at 60° for 20 min, the separation of the two bands remained unchanged (bands I and III were observed). These results indicate that a thermodynamically stable species, an associated ion pair ($\text{Ph}_3\text{C}^+\text{Y}^-$), was formed in 20% oleum and $\text{FSO}_3\text{H}-\text{SbF}_5$ (1:1 mole:mole) solutions at room temperature and in 100% H_2SO_4 + 20% oleum and 100% H_2SO_4 + $\text{FSO}_3\text{H}-\text{SbF}_5$ (1:1 mole:mole) superacid mixtures at higher temperature (60°). Further, the gegenion is relatively tightly bound and does not perceptibly exchange with the solvent at 25° .

It is interesting to note that the absorption spectrum of ion **1** in 20% oleum + $\text{FSO}_3\text{H}-\text{SbF}_5$ (1:1 mole:mole) superacid system at room temperature is similar to that observed in 100% H_2SO_4 but is different from that observed in each individual superacid system. However, it slowly changes to that observed in either 20% oleum or $\text{FSO}_3\text{H}-\text{SbF}_5$ (1:1 mole:mole) solution by warming the solution at 60° for 10 min. The unusual behavior of ion **1** in this superacid mixture may be explained by

(12) Free ions (or nonassociated ions) can only be observed in the gas phase (in a mass spectrometer). Ions formed in solution phase are always associated with the medium (or the gegenions) to a certain degree. In the lowest nucleophilicity superacid system, these associations are weak.

(13) G. A. Olah, R. H. Schlosberg, R. D. Porter, Y. K. Mo, D. P. Kelly, and Gh. D. Mateescu, *J. Amer. Chem. Soc.*, **94**, 2034 (1972).

the fact that reaction between $\text{FSO}_3\text{H}-\text{SbF}_5$ and 20% oleum occurs prior to the ionization of **2** and thus changes the nature of the gegenion. The chemistry of this superacid system has been reviewed recently by Gillespie and Peel.¹⁴

It seems clear, therefore, that the propeller-shaped structure of ion **1** is very sensitive to the nature of the gegenions. The degree of interaction between ion **1** and the gegenions or the ability to form an associated ion pair, $\text{Ph}_3\text{C}^+\text{Y}^-$, depends on the nature of the gegenions. Consequently the propeller-shaped structure of ion **1** is directly related to such interaction and thus alters the absorption and the MCD spectra. In summary, we have observed significant changes in the absorption and MCD spectra of ion **1** in various superacid media and have found three MCD bands in the near-uv and visible spectrum of ion **1**. It should be noted that Nemcova, Malat, and Zahradnik,¹⁵ in calculating the excitation energies and oscillator strengths of ion **1** using the semiempirical LCAO-SCF-CI method of Pariser, Parr, and Pople, found only two absorption maxima in the long wavelength region when they assumed that ion **1** has a planar confirmation.

Acknowledgment. We are indebted to the National Institutes of Health and the National Science Foundation for partial financial support and to Mrs. Ruth Records for technical assistance.

(14) R. J. Gillespie and T. E. Peel in "Advances in Physical Organic Chemistry," V. Gold, Ed., Academic Press, New York, N. Y., 1971, p 1.

(15) I. Nemcova, M. Malat, and R. Zahradnik, *Collect. Czech. Chem. Commun.*, **34**, 2880 (1969).

(16) Postdoctoral research fellow (1973-1974), supported in part by NIH Grant No. GM 06840.

Yoke K. Mo,¹⁶ Robert E. Linder, Günter Barth
Edward Bunnenberg, Carl Djerassi*

Department of Chemistry, Stanford University
Stanford, California 94305

Received February 19, 1974

Observation of a Second Wien Effect in Nonaqueous Solutions of Dichloro-1,1,7,7-tetraethyldiethylenetriaminenickel(II) and of Sodium Tetraphenylborate

Sir:

The enhanced dissociation of weak electrolytes by high electric fields, known as the second Wien or dissociation field effect,¹ was first accounted for theoretically by Onsager,² and the principal features of this theory have been verified by the available experimental data,³ most of which relate to simple inorganic salts in aqueous solution.^{4,5} Detailed investigations of the effect in nonaqueous media are rather rare.^{2,6} As well as being of interest from an electrochemical standpoint, the second Wien effect is the basis of the electric field-

(1) M. Wien and J. Schiele, *Z. Phys.*, **32**, 545 (1931).

(2) L. Onsager, *J. Chem. Phys.*, **2**, 599 (1934).

(3) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolyte Solutions," Reinhold, New York, N. Y., 1952.

(4) F. E. Bailey and A. Patterson, *J. Amer. Chem. Soc.*, **74**, 4426, 4428, 4756 (1952).

(5) M. Eigen and E. M. Eyring, *J. Amer. Chem. Soc.*, **84**, 3254 (1962); *Inorg. Chem.*, **2**, 636 (1963).

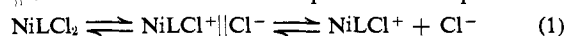
(6) D. J. Mead and R. M. Fuoss, *J. Amer. Chem. Soc.*, **61**, 2047 (1939); *ibid.*, **62**, 1720 (1940).

Table I. Second Wien Effects at 25°

	NaBPh ₄ /tetrahydrofuran ^a			NiLCl ₂ /acetonitrile ^b					
10 ⁶ K _a M		8.10 ^c				3.75 ^d			
Concentration × 10 ⁶ M		1.74			1.60				0.534
α		0.842			0.381				0.558
ΔE = (E - 8) kV cm ⁻¹	15	25	30	8	12	16	22	22	
10 ² ΔΔ/Δ ₀ , obsd	3.3	5.4	7.1	1.0	1.4	1.9	2.5	2.0	
10 ² ΔΔ/Δ ₀ , theory	2.97	5.22	7.56	0.92	1.39	1.85	2.54	2.04	

^a ε = 7.39. ^b ε = 35.95. ^c Reference 10. ^d Reference 8.

jump chemical relaxation method⁷ for the kinetic investigation of rapidly established ionic equilibria. We have recently used⁸ this method to study the kinetics of structural interconversion in dichloro-1,1,7,7-tetraethyl-diethylenetriaminenickel(II) (NiLCl₂, where L is the terdentate ligand Et₂N(CH₂)₂NH(CH₂)₂NEt₂). The complex exists in four- and five-coordinate modifications in acetonitrile⁹ and behaves as a moderately weak electrolyte in this solvent (Λ ~ 50 cm² mol⁻¹ Ω⁻¹ in 5 × 10⁻⁴ mol dm⁻³ solution), dissociating in two stages (1). NiLCl₂||Cl⁻ denotes a solvent-separated ion pair.



As well as providing kinetic information,⁸ the investigation presented an opportunity of testing the Onsager theory for a transition metal complex in a nonaqueous solvent. The latter aspect is the subject of the present communication. To the best of our knowledge, second Wien effects in such systems have not previously been reported. Measurements were also made on the system NaBPh₄ in tetrahydrofuran which also dissociates in two stages.¹⁰

The experimental technique is described in more detail elsewhere.⁸ The apparatus was originally designed for the determination of chemical relaxation times but it also permits the measurement of second Wien effects from the limiting amplitudes of the relaxation traces. A high voltage pulse of about 9 μsec duration was applied across an asymmetric Wheatstone bridge. Sample and reference cells with polished platinum electrodes (2.5 cm diameter) formed two arms of the bridge, the other two arms being low resistance terminations (20–50 Ω). The sample and reference cell resistances were in the range (3–7) × 10³ Ω, and the reference cell contained a strong electrolyte (~10⁻⁴ mol dm⁻³ solution of NaBPh₄ in acetonitrile) to cancel conductance changes arising from the first Wien effect.^{11,12} In practice this was achieved by comparing the output signals from the sample and reference arms of the bridge on an oscilloscope (Hewlett-Packard 181A) fitted with a sensitive differential amplifier (type 1803A). The second Wien conductance change in the sample on applying a high-field pulse was then recorded on the oscilloscope as the out-of-balance signal from the differential amplifier.

(7) (a) M. Eigen, *Discuss. Faraday Soc.*, **17**, 194 (1954); (b) M. Eigen and L. DeMaeyer in "Technique of Organic Chemistry," Vol. VIII, Part II, S. L. Friess, E. S. Lewis, and A. Weissberger, Ed., Interscience, New York, N. Y., 1963, p 898; (c) E. M. Eyring, *Surv. Progr. Chem.*, **2**, 57 (1964).

(8) H. Hirohara, K. J. Ivin, J. J. McGarvey, and J. Wilson, *J. Amer. Chem. Soc.*, in press.

(9) Z. Dori and H. B. Gray, *J. Amer. Chem. Soc.*, **88**, 1394 (1966).

(10) J. Comyn, F. S. Dainton, and K. J. Ivin, *Electrochim. Acta*, **13**, 1851 (1968).

(11) M. Wien, *Ann. Phys.*, **83**, 327 (1927).

(12) According to Wilson's theory of the first Wien effect (ref 3, p 128), it is estimated that the magnitude of the effect under our conditions is, at most, 0.4% of Δ₀ (i.e., 0.4% of (V_E - V₈)).

The Onsager theory is only valid when the applied field is sufficient to destroy the ionic atmosphere completely around each ion.⁸ This corresponds approximately to the field at which the increase in conductance becomes just measurable, in the present systems, 8 kV cm⁻¹. The procedure was therefore first to adjust the electrolyte concentration in the reference cell until the bridge was balanced on applying a field pulse of 8 kV cm⁻¹. The reference cell conductance at this field strength was not determined directly. Instead the channel of the differential amplifier connected to the sample cell was grounded and the amplitude of the 8 kV cm⁻¹ pulse was measured on the oscilloscope as the signal, V₈, developed across the voltage divider circuit formed by the reference cell resistance and the low resistance termination. V₈ is proportional to (field strength) × (reference cell conductance at 8 kV cm⁻¹). A field pulse, E, greater than 8 kV cm⁻¹ was then applied across the whole bridge and the small, rapid voltage change that developed, as a result of the second Wien effect in the sample, was recorded. The maximum amplitude, ΔV_{ΔE}, of this voltage change is proportional to (increase in field strength, ΔE) × (conductance change in sample associated with ΔE). Finally the voltage, V_E, proportional to the reference cell conductance at field strength E was determined by the same procedure as described for V₈. Since (V_E - V₈) measures the cell conductance in the absence of a second Wien effect as the field is increased from 8 to E kV cm⁻¹, the fractional change, ΔΔ/Δ₀, in the sample cell conductance due to second Wien effects alone is given by the ratio ΔV_{ΔE}/(V_E - V₈). This procedure for obtaining ΔΔ/Δ₀ has the advantage that it does not require the value of the conductance at high field, which is difficult to measure, although the results, since they depend on the reading of oscilloscope traces, are not very precise.

The results are presented in Table I. The theoretical values were calculated from the Onsager equation (2) for a binary electrolyte.²

$$\frac{\Delta\Delta}{\Delta_0} = 9.636z^3 \frac{(1 - \alpha) \Delta E}{(2 - \alpha) \epsilon T^2} \quad (2)$$

where z is the valency of the ion, α is the degree of dissociation, ε the relative permittivity of the solvent, and T the temperature.

The experimental values are in good agreement with the theory showing that, for both systems, a field of 8 kV cm⁻¹ is sufficient to effect complete breakdown of the ionic atmospheres. It is interesting that the agreement between experiment and theory is good despite the differences in α, the differing shapes of the ions (the Onsager theory assumes a spherical shape), and the two-step nature of the dissociation in both systems. This last point is significant in that the Onsager theory

assumes the very rapid establishment of equilibrium between molecules and ion pairs in the coupled equilibria, molecules \rightleftharpoons ion pairs \rightleftharpoons free ions, and we therefore conclude that in our systems the formation of the loose ion pair from the tight ion pair is not rate determining. This agrees with the conclusions reached from our kinetic studies⁸ on NiLCl₂.

Hideo Hirohara, Kenneth J. Ivin, John J. McGarvey*

Department of Chemistry, The Queen's University of Belfast
Belfast BT9 5AG, Northern Ireland

Received January 3, 1974

²³Na Quadrupole Coupling Constants in Different Coordination Shells from ²³Na and ¹³C Fourier Transform Nuclear Magnetic Resonance Measurements on Sodium Cryptates

Sir:

Ionic solvation has been investigated by many research groups using most of the available electrochemical and spectroscopic methods, including nuclear magnetic resonance spectroscopy.¹ Among metal cations, much work has been done on the sodium cation by direct observation on the ²³Na nmr chemical shifts and quadrupolar broadening effects.²⁻¹³

Knowledge of ²³Na quadrupolar coupling constants, $\chi_{Na} = (e^2qQ/h)$ ($eQ = ^{23}\text{Na}$ nuclear quadrupole moment), and electric field gradients, eq in various coordination states, would be of much interest to the understanding of the nature of cation solvation, but such determinations are hampered by the uncertainties in solvation number¹⁴ and the fluctuation of the coordination sphere.

Stable sodium complexes with well-defined coordination shells provide a unique way to study the solvated cation, as shown by recent ²³Na studies¹⁵⁻¹⁷ of Na⁺ complexes of natural¹⁵ and synthetic¹⁸ macrocyclic ligands.

(1) J. F. Hinton and E. S. Amis, *Chem. Rev.*, **67**, 367 (1967); U. Mayer and V. Gutman, *Struct. Bonding (Berlin)*, **12**, 113 (1972); C. Deverell, *Progr. Nucl. Magn. Resonance Spectrosc.*, **4**, 235 (1969).

(2) O. Jardetzky and J. E. Wertz, *J. Amer. Chem. Soc.*, **82**, 318 (1960).

(3) G. A. Rechnitz and S. B. Zamochnick, *J. Amer. Chem. Soc.*, **86**, 2953 (1964).

(4) (a) C. Deverell and R. E. Richards, *Mol. Phys.*, **10**, 551 (1966);

(b) C. Deverell, *ibid.*, **16**, 491 (1969); (c) C. Hall, R. E. Richards, G. N. Schulz, and R. R. Sharp, *ibid.*, **16**, 529 (1969).

(5) M. Eisenstadt and H. L. Friedman, *J. Chem. Phys.*, **46**, 2182 (1967).

(6) V. S. Griffiths and G. Socrates, *J. Mol. Spectrosc.*, **27**, 358 (1968).

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

(8) V. I. Ionov, R. K. Mazitov, and I. I. Evdokimov, *Zh. Strukt. Khim.*, **10**, 208 (1969).

(9) T. L. James and J. H. Noggle, *Proc. Nat. Acad. Sci. U. S.*, **62**, 644 (1969); *J. Amer. Chem. Soc.*, **91**, 3424 (1969).

(10) R. H. Erlich, E. Roach, and A. I. Popov, *J. Amer. Chem. Soc.*, **92**, 4989 (1970); R. H. Erlich and A. I. Popov, *ibid.*, **93**, 5620 (1971); M. Herlem and A. I. Popov, *ibid.*, **94**, 1431 (1972); R. H. Erlich, M. S. Greenberg, and A. I. Popov, *Spectrochim. Acta, Part A*, **29**, 543 (1972).

(11) R. D. Green and J. S. Martin, *Can. J. Chem.*, **50**, 3935 (1972).

(12) G. J. Templeman and A. L. Van Geet, *J. Amer. Chem. Soc.*, **94**, 5578 (1972); A. L. Van Geet, *ibid.*, **94**, 5583 (1972).

(13) G. W. Canters, *J. Amer. Chem. Soc.*, **94**, 5230 (1972).

(14) E. S. Amis and J. F. Hinton, *Chem. Rev.*, **71**, 627 (1971).

(15) D. H. Haynes, B. C. Pressman, and A. Kowalsky, *Biochemistry*, **10**, 852 (1971).

(16) A. M. Grotens, J. Smid, and E. De Boer, *Chem. Commun.*, 759 (1971).

(17) E. Shchori, J. Jagur-Grodzinski, Z. Luz, and M. Shporer, *J. Amer. Chem. Soc.*, **93**, 7133 (1971); E. Shchori, J. Jagur-Grodzinski, and M. Shporer, *ibid.*, **95**, 3842 (1973).

(18) C. J. Pedersen and H. K. Frensdorff, *Angew. Chem.*, **84**, 16 (1972); *Angew. Chem., Int. Ed. Engl.*, **11**, 16 (1972).

Macrobicyclic ligands¹⁹ forming cryptate-type cation inclusion complexes,²⁰ in which the coordination shell entirely surrounds the cation, should be well suited for such studies since these complexes are much more stable²¹ than the macrocyclic ones and cation exchange is slower (see below).

We present here the results of a study of ²³Na nuclear quadrupolar coupling constants in four "frozen" coordination shells containing as binding sites two nitrogens and four, five, or six oxygens or four oxygens and two sulfurs, *i.e.*, the sodium cryptates of ligands 1, 2, 3, and 4, respectively. Assuming zero asymmetry parameter, the quadrupolar relaxation time T_q of the ²³Na nucleus is given by eq 1²² (nuclear spin of ²³Na =

$$T_q^{-1} = \pi \Delta\nu = (2\pi^2/5)(e^2qQ/h)^2\tau_c \quad (1)$$

^{3/2}). χ_{Na} may be calculated from the line width $\Delta\nu$ of the ²³Na resonance if the rotational correlation time, τ_c , of the motions of the sodium complex is known. Since τ_c values estimated in the usual way from the molecular radius and Debye's relation may be in error (generally too long) by one order of magnitude,²³ we employed an indirect *double nuclear spin probe* method.^{24,25}

Using the dipole-dipole relaxation equation (2) one

$$T_1^{-1}(^{13}\text{C}) = n^2\hbar^2 \gamma_H^2\gamma_C^2 r_{CH}^{-6} \tau_c = 4.4046 \times 10^{10} \tau_c \quad (2)$$

$$(n = 2 \text{ for a CH}_2 \text{ group; } r_{CH} = 1.085 \pm 0.005 \text{ \AA})$$

may obtain τ_c from the ¹³C relaxation times T_1 (¹³C) of the CH₂ carbons of the sodium cryptates. Then, making the reasonable assumption that, in the quite rigid complexes, τ_c (from ¹³C data) also represents the reorientational motions which modulate the ²³Na quadrupolar interaction, one may introduce τ_c in eq 1 and calculate χ_{Na} from $\Delta\nu$. The ¹³C nmr spectra and relaxation times and the ²³Na spectra have been measured by the Fourier transform technique. Spectral data and results calculated with eq 1 and 2 are given in Table I.²⁶

The correlation times of the four cryptates (Table I) are about a factor of 5 shorter than those which are cal-

(19) B. Dietrich, J. M. Lehn, J. P. Sauvage, and J. Blanzat, *Tetrahedron*, **29**, 1629 (1973); B. Dietrich, J. M. Lehn, and J. P. Sauvage, *Chem. Commun.*, 1055 (1970).

(20) B. Dietrich, J. M. Lehn, and J. P. Sauvage, *Tetrahedron*, **29**, 1647 (1973).

(21) J. M. Lehn and J. P. Sauvage, *Chem. Commun.*, 440 (1970), and unpublished results; J. M. Lehn, *Struct. Bonding (Berlin)*, **16**, 1 (1973).

(22) A. Abragam, "The Principles of Nuclear Magnetism," Clarendon Press, Oxford, 1961, Chapter 8.

(23) W. B. Moniz and H. D. Gutowsky, *J. Chem. Phys.*, **38**, 1155 (1962).

(24) J. M. Lehn and J. P. Kintzinger in "Nitrogen N.M.R.," M. Witanowski and G. A. Webb, Ed., Plenum Press, London, 1973, Chapter 3, and references therein.

(25) J. P. Behr and J. M. Lehn, *Biochem. Biophys. Res. Commun.*, **49**, 1573 (1972); J. R. Lyerla, Jr., D. M. Grant, and R. K. Harris, *J. Phys. Chem.*, **75**, 585 (1971).

(26) The solutions contained stoichiometric amounts of a given ligand and NaCl (0.25 M each) in methanol-D₂O 95/5. Since the stability constants are very high in this medium (>10⁸),²¹ the solution contains only the sodium cryptates. The spectra have been measured at 25.1 MHz for both ¹³C (with ²D lock) and ²³Na (without field-frequency lock and by decreasing slightly the magnetic field). The ¹³C relaxation times have been obtained using the inversion-recovery method. The short relaxation times measured (about 1 sec), the size of the molecules and the presence of two protons on each carbon justify the use of eq 2. Indeed the relaxation of these carbon nuclei may be expected to occur almost exclusively *via* the dipole-dipole mechanism (for a discussion see, for example, G. C. Levy, *Accounts Chem. Res.*, **6**, 161 (1973)).