cm^{-1}).[4] For these and other reasons, we assume a Be–N bond with the beryllium atom in a roughly trigonal environment (two borohydride groups and one trimethylamine).

The net result of forming the trimethylamine 1:1 adduct of beryllium borohydride is to produce an increased ionic character in the borohydride group. This is indicated (*vide supra*) by observed shifts of the two terminal B–H stretches and BeH_2B asymmetric bridge stretch, which shift toward the single B–H stretching frequency of the borohydride ion at 2270–2320 cm^{-1}.[4] Similarly, the BH deformation modes and the BeH_2B symmetric bridge stretch shift toward the single B–H deformation frequency of the free borohydride ion at 1080–1096 cm^{-1}.[4]

Comparsion of the spectra of beryllium borohydride and the 1:1 trimethylamine adduct indicates the absence of terminal Be–H groups in these compounds. Because two independent studies have established that the terminal Be–H stretching mode occurs in the 1740–1807-cm^{-1} region, one reasonably expects a Be–H terminal group to have an absorption in the 1600–2000-cm^{-1} region.[31,32] Since the nitrogen is bound to the beryllium, one would expect a significant decrease in the Be–H terminal stretching frequency if such a terminal group *were* present. No such Be–H terminal group is indicated by these data.

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Reaction of Xenon Difluoride with Aromatic Compounds. II. The Use of Xenon Difluoride as a Selective Fluorinating Agent[1a]

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Abstract: Xenon difluoride is shown to react with a variety of substituted benzenes in CCl_4 or CH_2Cl_2 to produce fluorobenzenes in good yield. The reaction is catalyzed by HF and does not proceed without it. Substituent effects are similar to those observed in electrophilic aromatic substitution reactions. The use of xenon difluoride often offers an attractive alternative route to the conventional Balz–Schiemann reaction for the preparation of fluorinated aromatic compounds.

One of the most interesting problems in organic fluorine chemistry has been the lack of a general selective fluorinating agent for aromatic compounds. It has been stated that "Fluorine differs from other halogens in that it cannot be introduced into an aromatic ring by direct reaction because of its great reactivity. This has necessitated the development of special methods and has been both difficult and slow."[2] In a few isolated experiments, ring fluorination of suitably activated compounds has been achieved without loss of aromaticity. For example, reaction of 2,4-dinitroaniline with fluorine in HF gave small yields of 1-difluoroamino-5-fluoro-2,4-dinitrobenzene.[3] Fluoroxytrifluoromethane (CF_3OF) reacts with salicylic acid to give a 4:1 mixture of 3- and 5-fluorosalicylic acid in 70% yield.[4] Most reactive fluorinating agents such as fluorine,[5] high-valency metal fluorides,[6] and halogen fluorides[7] yield mostly fluorine addition products and tars, although it has been reported that ClF_3 in the presence of CoF_2 reacts with substituted benzenes to give about a 20% yield of fluoro substitution products.[7]

Recently, however, Grakauskas has shown that fluorine, in solution and well below room temperature, can be used to effect electrophilic substitution reaction.[8] The difficulty with known fluorinating agents in effecting electrophilic aromatic substitution is certainly related to the difficulty in forming F^+ (ionization potential of F = 401.5 eV; ionization potential of Cl = 300 eV).[9] An alternative explanation for the lack of selectivity in the reactions of strong fluorinating agents may involve the thermodynamics of the reac-

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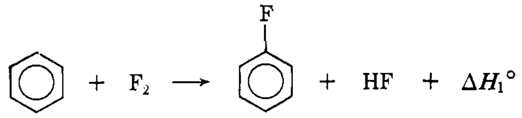
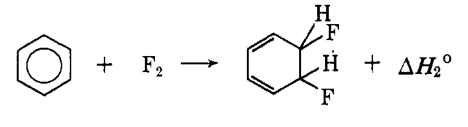
Table I. Yields and Isomers Formed in the Fluorination with XeF_2

R-C_6H_5	% yield RC_6H_4F[a]	Isomer distribution, %			Rel ratio,[b] o/m/p	HF generated / XeF_2 added
		Ortho	Meta	Para		
OCH_3	65.4	30.5	2.5	32.4	12.2/1.0/25.9	1.25
CH_3	32.4	16.1	2.6	13.7	6.2/1.0/10.5	1.25
Cl	65.5	16.0	3.2	46.3	5.0/1.0/29.0	1.10
F	46.9	11.8	2.8	32.3	4.2/1.0/23.0	1.22
H	68.0					1.24
CF_3	75.5	0	71.7	3.8	0/9.4/1.0	1.11
NO_2	81.2	18.9	50.9	11.4	1.0/2.7/1.2	1.21

[a] Based on the amount of aromatic compound that reacted. [b] Corrected for two ortho and two meta positions.

tions involved. Specifically, it is of interest to examine the enthalpy of reaction for the following two processes.


(1)


(2)

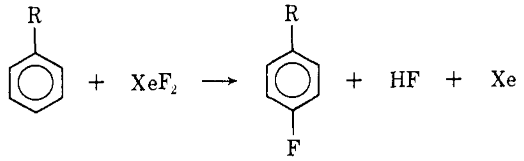
Using available thermodynamic data,[10] $\Delta H_1°$ is calculated to be -126.3 kcal/mol and $\Delta H_2°$ is estimated to be about -141.8 kcal/mol. Thus, addition of fluorine to the aromatic ring appears to be more exothermic by about 15.5 kcal/mol than is substitution of F for H.

We recently reported[11] that xenon difluoride reacts with benzene in CCl_4 to produce fluorobenzene in 68% yield.[11] Small amounts of biphenyl, 2- and 4-fluorobiphenyl, and tars are also formed. The reaction was catalyzed by HF and did not proceed without it. A mechanism of fluorination involving a benzene radical cation was proposed. We have reported the results of an esr investigation of the reaction which demonstrated that 4,4′ disubstituted polyphenyl radical cations were formed.[12] The purpose of this paper is to confirm the value of XeF_2 as a reagent which will effect electrophilic aromatic substitution of fluorine for hydrogen in good yield.

Results

The results of the reaction of XeF_2 with several substituted benzenes are listed in Table I. The yields of monofluoro-substitution products are rather high. Small amounts of biphenyls, fluorobiphenyls, and tars are formed as by-products Substituent effects appear to be similar to those observed in electrophilic aromatic substitution reactions.[13] In all cases, an examination of the reaction products using mass spectroscopic and infrared absorption techniques indicated the absence of fluorine addition products (fluorinated cyclohexadienes, cyclohexenes, and cyclohexanes). Of particular interest is the observation that side-chain-substitution products such as benzyl fluoride were not found in the reaction of XeF_2 with toluene.

One mole of Xe is liberated per mole of XeF_2. All reactions are catalyzed by HF and do not take place without it. The data in Table I indicate that about 1 mol of HF is formed per mole of XeF_2 added. The reaction is thus autocatalytic and appears to proceed according to the following stoichiometry.



The small excess of HF generated (Table I) probably arises from the fact that 2 mol of HF per mole of XeF_2 added is formed when XeF_2 reacts with the aromatic compound to form a biphenyl.

Compounds containing strong electron-withdrawing groups generally require more HF for initiation of the reaction. Over 50 times as much HF is necessary for initiation in the fluorination of benzotrifluoride as with toluene. The reaction is conveniently monitored either by following the increase in pressure due to xenon evolution or by observing the disappearance of XeF_2 crystals in the bottom of the reaction vessel. The reactions studied were run both in CCl_4 and CH_2Cl_2 and, as shown in Table II, no significant difference in the products was observed. However, the use of HF as a solvent resulted in considerably more tar with diminished yield of the fluoro-substituted benzene.

Table II. Solvent Effect on the Fluorination Reaction

R-C_6H_5	Solvent	% yield RFC_6H_4	Isomer distribution, %			% tar
			Ortho	Meta	Para	
F	CCl_4	47.0	11.8	2.8	32.2	53.0
F	CH_2Cl_2	52.2	14.0	3.2	35.0	47.8
H	CCl_4	68.0				32.0
H	CH_2Cl_2	52.0				48.0
CF_3	CCl_4	75.0	0	71.7	3.8	24.5
CF_3	CH_2Cl_2	79.6	25.0	43.5	11.1	20.4
CF_3	HF	50.0	12.8	33.4	3.8	50.0
NO_2	CCl_4	67.9	14.5	41.8	11.6	32.1
NO_2	CH_2Cl_2	81.2	18.9	50.9	11.4	22.0

The reaction possesses several advantages over current methods for preparing monofluorinated aromatic compounds. The conversion requires only

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Table III. Experimental Variables in the Fluorination Reaction

R-C_6H_5	RC_6H_5 added, mmol	XeF_2 added, mmol	HF added, mmol	Solvent	Solvent, g	Reaction temp, °C	Reaction time (tot), hr	Reaction color
OCH_3	40.4	13.23	1.0	CCl_4	16.3	*ca.* −20	2.1	Blue
Cl	32.9	10.86	5.0	CCl_4	11.1	25	5.0	Blue
NO_2	18.8	6.1	18.0	CCl_4	5.4	25	48	Orange then black
NO_2	43.2	9.3	14.9	CH_2Cl_2	8.3	25	0.6	Crimson
F	43.2	14.2	2.2	CH_2Cl_2	13.2	25	5.5	Green
F	8.9	9.0	1.4	CCl_4	13.8	25	2.7	Green
H	22.1	7.8	4.0	CH_2Cl_2	16.5	25	1.25	Green
H	26.5	7.3	1.1	CCl_4	14.7	25	3.2	Green
CF_3	31.9	10.9		HF	8.1	−10 to −75	0.33	Green then purple
CF_3	32.5	10.1	1.6	CCl_4	15.0	25	3	Purple
CF_3	7.3	7.6	5.4	CH_2Cl_2	12.8	25	24	Yellow
CH_3	57.6	19.7	0.6	CCl_4	15.8	25	2.0	Green then purple

one step. For example, *m*-fluorobenzotrifluoride is usually prepared from benzotrifluoride in a three-step process involving nitration, reduction, and diazotization in a maximum yield of 56.5%.[14] However, fluorination with XeF_2, in one step, results in about a 72% yield. In practice, all the reagents except HF are combined, HF is added, and the temperature is controlled (by cooling) so that reaction is complete in 2–3 hr. Sufficient column technology now exists so that the various isomers (except two, see Experimental Section) may be conveniently separated.

Xenon difluoride is commercially available,[15] but also can be prepared readily either by thermal means (in large quantities)[16] or photochemically (in small quantities).[17] The fluorine used in the preparation of XeF_2 can be handled in either a copper or a dry Pyrex apparatus. Although xenon is rather expensive (~$5/g), it can be quantitatively recovered after the fluorination reaction, refluorinated to XeF_2, and reused.

As a further example of the usefulness of XeF_2 as a fluorinating agent, the compound 1-fluoro-2,4,6-trineopentylbenzene was synthesized. Attempts to obtain this compound (needed for a study on hindered rotation) by diazotization of the corresponding amine resulted in ring closure to give an indane.[18] Reaction of xenon difluoride with 1,3,5-trineopentylbenzene in CCl_4 resulted in a 41% yield of 1-fluoro-2,4,6-trineopentylbenzene (determined gas chromatographically). The remainder of the product was composed of several components which have not been characterized. A small sample was purified by fractional sublimation, preparative gas chromatography, and recrystallization, for characterization by infrared, nmr, mass spectroscopic, and elemental analysis.

Conclusion

Xenon difluoride has been shown to be a useful fluorinating agent which can be used to effect electrophilic substitution in aromatic compounds in good yield. The probable mechanisms involved will be discussed elsewhere.

Experimental Section

Reagents. Xenon difluoride was prepared and initially purified according to the procedure of Schreiner *et al.*[16] The XeF_2 was further purified from any HF by distillation onto anhydrous NaF. The mixture was heated for 2 hr at 60° and then several heads were flashed off, after which the XeF_2 was cooled to −75° and evacuated to 10^{-6} Torr. Using this procedure an 86% yield of pure XeF_2 was obtained. The HF had a conductivity of 5×10^{-6} mhos at 0°. Benzene (99.999%), nitrobenzene (99.9%), and toluene (99.9%) used were obtained from James Hinton Co., Newport News, Va. All other materials, originally of commercial grade, were dried over anhydrous $MgClO_4$ and fractionally distilled over anhydrous Na_2SO_4 under an atmosphere of dry argon.

Instrumentation. Melting points were obtained on a Fisher-Johns apparatus and are uncorrected. Nuclear magnetic resonance spectra were obtained using Varian HA-100, and HR-220 megahertz equipment. Infrared spectra were obtained using a Beckman IR-12 spectrometer and matched 0.1-mm KBr cells. Mass spectra were obtained using a Perkin-Elmer Model 900 instrument and a Bendix time-of-flight mass spectrometer. An F and M Model 5750 gas chromatograph, equipped with both thermal conductivity and flame ionization detectors, was used.

Reaction Procedure. The following general reaction procedure was used to prepare and identify compounds produced by reaction of XeF_2 with aromatic compounds. The specific experimental variables for each reaction are listed in Table III. The procedure to be described was used in order to avoid contamination by any foreign substances (O_2, H_2O, etc.).

Approximately 1–2 g of XeF_2 was transferred to a 29-cc Kel-F tube. To a second tube containing anhydrous Na_2SO_4, 3 mol of the aromatic compound per mole of XeF_2 used and enough CCl_4 or CH_2Cl_2 to give about a 15% solution were added. Both tubes were connected to a Kel-F line which was connected to a Monel vacuum line. The tube containing the XeF_2 was cooled to −75° and evacuated to 5×10^{-6} Torr. The tube containing the organic solution was degassed by the freeze–thaw technique until a pressure change after freezing to −110° was less than 10^{-5} Torr. The organic solution was then distilled or poured *in vacuo* into the Kel-F tube containing the XeF_2 at −196°. Upon warming to room temperature, no reaction was observed. After cooling to −75°, hydrogen fluoride (measured tensimetrically) was added until reaction began when the solution was warmed. Bright colors were always observed when reaction commenced. CAUTION! If the reaction is run in a closed system, care *must* be taken to allow sufficient ballast volume so that the pressure does not rise above 2 atm. Xenon evolution frequently becomes so rapid that application of a Dry Ice bath is necessary to prevent the reaction solution from entering the ballast volume. In this respect, it was found that a solvent was advantageous. With compounds having electron-donating substituents such as anisole or toluene, methylene chloride (fp −97°) was used; otherwise carbon tetrachloride was satisfactory. After reaction was complete, the vapor phase was condensed in the reaction tube at −196°. These materials were warmed to −75° and the Xe evolved was transferred to a storage can. The resulting solution was distilled at 25° into a second Kel-F tube. Excess 1.000 *M* aqueous NaOH was added to the distillate

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Table IV. Columns Used in the Separation of Fluorinated Products

Column	Specifications
A	8 ft × $^1/_8$ in., 5% diethylene glycol succinate on Chrom W (80–100 mesh)
B	15 ft × $^3/_{16}$ in., 5% B,B′-oxydipropionotrile on Chrom G (60–80 mesh)
C	6 ft × $^1/_8$ in., 3% silicone fluid SF96 on Chrom W (80–100 mesh)
D	6 ft × $^1/_8$ in., 5% tricresyl phosphate on Chrom W (80–100 mesh)
E	32 ft × $^1/_4$ in., 3% QF-1 on Chrom (60–80 mesh)
F	20 ft × $^1/_8$ in., 5.2% diethylene glycol succinate on Chrom G (80–100 mesh)
G	20 ft × $^1/_8$ in., 6.1% tetracyanoethylated pentaerythritol on Chrom (80–100 mesh)

Table V. Retention Times of Fluorinated Benzenes

Compound	Time,[a] min	Column	Temp, °C	Flow rate, cc/min
m-Fluoronitrobenzene	4.00	A	152	30
p-Fluoronitrobenzene	5.00	A	152	30
Nitrobenzene	6.10	A	152	30
o-Fluoronitrobenzene	7.40	A	152	30
m-Chloronitrobenzene	10.00	A	152	30
p-Chloronitrobenzene	11.40	A	152	30
o-Chloronitrobenzene	14.10	A	152	30
m-Fluorobenzotrifluoride	0.55	B	62	38
p-Fluorobenzotrifluoride	1.35	B	62	38
Benzotrifluoride	1.60	B	62	38
o-Fluorobenzotrifluoride	3.95	B	62	38
m-Chlorobenzotrifluoride	5.80	C	75	18
p-Chlorobenzotrifluoride	6.55	C	75	18
o-Chlorobenzotrifluoride	10.65	C	75	18
3,3′-Ditrifluoromethylbiphenyl	4.25	C	175	30
m-Difluorobenzene	2.07	D	43	30
Fluorobenzene	2.90	D	43	30
p-Difluorobenzene	3.65	D	43	30
o-Difluorobenzene	4.60	D	43	30
Toluene	4.15	E	73	54
o-Fluorotoluene	5.30	E	73	54
m- + *p*-Fluorotoluene	6.20	E	73	54
Anisole	4.2	D	110	25
m-Fluoroanisole	4.2	D	110	25
p-Fluoroanisole	4.7	D	110	25
o-Fluoroanisole	5.5	D	110	25
m-Fluorochlorobenzene	2.5	D	12	27
Chlorobenzene	3.3	D	92	27
p-Fluorochlorobenzene	3.3	D	92	27
o-Fluorochlorobenzene	4.1	D	92	27

[a] Retention time from CH_2Cl_2.

and was later titrated to determine the amount of HF generated. After drying the resultant solution over Na_2SO_4, the products were analyzed in the following manner. By comparison of the infrared spectra of known compounds with that of the distillate, it was found that bands associated with ortho-, meta-, and para-fluoro-substituted benzenes were observable in the reaction distillate. By comparison of the gc retention times of pure samples of fluorobenzenes (on columns which separated the ortho-, meta-, and para-fluoro isomers) with the peaks observed in the distillate, the products were further characterized. Peak areas were determined using a Disc integrator and then compared to a calibration curve which was obtained by using solutions of known concentration. In this manner, yields and isomer ratios were determined. It was possible to conduct these reactions within a mass balance of about 5% when CH_2Cl_2 was the solvent, and within 1% with CCl_4. Since the separation of many of the fluorinated isomers formed has not previously been reported, the columns used for these analyses and various retention times for the isomers present are listed in Tables IV and V. To further characterize the fluorination products, the distillate was chromatographed on the appropriate column and a mass spectrometer was used as the detector. In this manner, it was found that each peak consisted of a single component and had the correct parent ion mass and fragmentation pattern expected for the particular monofluoro-substituted benzene.

It was not possible to separate either anisole from *m*-fluoroanisole or *m*- from *p*-fluorotoluene. In the former case, the 855-cm^{-1} absorption band was used to estimate the per cent *m*-fluoroanisole formed. In the latter case, the 500-cm^{-1} band for *p*-fluorotoluene and the 1140-cm^{-1} band for *m*-fluorotoluene were used to determine the para to meta ratio.

Preparation of 1-Fluoro-2,4,6-trineopentylbenzene. Trineopentylbenzene (TNB) (0.777 g) in CCl_4 (9.535 g) was added to 1.137 g of XeF_2 in a Kel-F tube. The solution was degassed by the freeze–thaw technique. At −75°, 6.4 × 10^{-4} mol of HF was added and the solution brought to room temperature. Reaction progressed as evidenced by an even slow evolution of Xe. The reaction was allowed to run overnight at 25° to give a dark brown solution. All of the XeF_2 had disappeared and 1 mol of Xe gas was evolved per mole of XeF_2 added. The resulting solution was washed with 10 ml of 1.0 *M* NaOH and dried over Na_2SO_4. By titration, it was found that 0.985 mol of HF was generated per mole of XeF_2 added. The CCl_4 was removed, leaving 0.782 g of brown oil. The oil was then sublimed at 0.1 mm and 81.2°, and 0.211 g of semisolid was collected. Chromatography of this material, using both a 6-ft × $^1/_8$-in. carbowax column and a 6-ft × $^1/_8$-in. SF96 column at 153° with a helium flow of 30 cc/min, revealed the presence of 13 components. Four components constituted the majority of the sublimate and had the following percentages: no. 2, 2.1, no. 5, 10; no. 6, 75; and no. 11, 12%.

The sublimate was further purified by preparative gc using an 8-ft × 0.5-in. 20% carbowax 20 M column at 182°, flow 80 cc/min. From this separation, 0.209 g of the major component was collected. It was then analyzed by gc using a 6-ft × $^1/_8$-in. UCW 98 column at 180° and found to contain *ca.* ten components and about 73% of one component. This mixture was injected into a gas chromatograph with a mass spectrometer as the detector. The mass spectrum of each peak was taken. It was found that several components have the CH_2F group but not the major component. The principal peaks in the mass spectrum of the main component are listed in Table VI. The fragmentation patterns closely parallel those of 2,4,6-trineopentylbenzene,[19] with the only difference being the presence of an additional 19 mass units. A 273 mass (TNFB-CH_2F) was not observed, as in the other fractions. A very strong 138 peak was observed and no 119 or 120 peak was found, which indicates that the fluorine is located on the ring. Then, 0.160 g of this mixture was centrifuged and 90 mg of a white solid was obtained (mp 53–54°). Recrystallization of this white powder from methanol yielded white crystals, mp 77–78°. A second recrystallization raised the melting point to 81.5–82° and yielded 0.0158 g of material. A third recrystallization did not change the melting point. Analysis of this twice-recrystallized solid on the UCW98 column indicated about 99.8% purity (by relative areas). The nmr spectrum (100-MHz) of TNFB consisted of a singlet at τ 9.11 (9-H from *t*-butyl group para to F), a singlet at 9.09 (18-H from two *t*-butyl groups ortho to F), a singlet at 7.62 (2-H from one CH_2 group para to F), a doublet at 7.52, J_{HF} = 2 cps (4-H, two CH_2 groups ortho to F), and a doublet at 3.35, J_{HF} = 7.4 cps (2-H, aromatic). The 220-MHz nmr spectrum of TNFB confirmed the above assignments. The ir spectrum (CCl_4) exhibited bands at 2930–2970 (s), 2910 (s), 2879 (s), 1615 (w), 1480 (s), 1465 (s), 1448

Table VI. Principal Peaks in the Mass Spectrum of 2,4,6-Trineopentylfluorobenzene

Mass	Species
306	TNFB
291	TNFB-CH_3
250	TNFB-*t*-butyl + H
249	TNFB-*t*-butyl
193	TNFB-2-*t*-butyl + H
192	TNFB-2-*t*-butyl
177	TNFB-2-*t*-butyl-CH_3
138	TNFB-3-*t*-butyl + 3H
97	*t*-Butyl

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(19) P. Martinson, *Acta Chem. Scand.*, **23**, 751 (1969).

(m), 1433 (m), 1395 (m), 1366 (s), 1336 (w), 1311 (w), 1298 (w), 1239 (m), 1215 (s), 1204 (m), 1170 (m), 1128 (m), 1080 (m), 948 (m), and 882 cm^{-1} (m).

Anal. Calcd for $C_{21}H_{35}F$: C, 82.35; H, 11.44; F, 6.20. Found: C, 82.29; H, 11.38; F, 6.50.

Acknowledgment. We are grateful to Drs. L. Kaplan, K. Wilzbach, and M. Studier for their assistance in the mass spectrometric identification of the compounds prepared.

Electrical Conductance of Anhydrous Potassium, Magnesium, Cobalt, Nickel, Copper, and Zinc *m*-Benzenedisulfonates in Methanol at 25°

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Abstract: The equivalent conductivities of the K^+, Mg^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} *m*-benzenedisulfonates have been measured in anhydrous methanol at 25°. The data for the 2:2 salts have been interpreted by the Fuoss–Kraus technique for determining the limiting equivalent conductance and association constant. The data for K_2-BDS have been analyzed by the Fuoss–Edelson technique obtaining the limiting conductance Λ_0 and therefore $\lambda^0{}_{1/2\mathrm{BDS}^{2+}}$ from the known conductance of K^+ in methanol. The values of $\lambda^0{}_{1/2\mathrm{Me}^{2+}}$ for Mg^{+2} and Zn^{2+} compare favorably with the data of Hartley and Raykes. With the so-determined values of Λ_0, the Fuoss–Onsager equation is fitted to the data as a two-parameter equation in the association constant K_A and collision diameter a. The sum of the Stokes hydrodynamic radii ($R_+^0 + R_-^0$) is of the same order of magnitude as a_J.

It is about 100 years since the pioneering measurements of ac electrical conductivity by Kolhrausch were performed in aqueous solutions of electrolytes. During this time the Onsager theory[2] at different levels of sophistication[3] has given a rather exhaustive microscopic picture of the phenomenon of conduction, at least in the diluted range. Other nonelectrochemical methods have been developed in the meantime, like nmr relaxation,[4] ultrasonic absorption, and other relaxation methods,[5] uv, visible,[6a] and Raman spectra.[6b] These techniques have offered intimate insights into the phenomena of solvent exchange in the first coordination sphere of the metal cation,[4] of the mechanism of ligand substitution during the process of complexation,[5] and of the coordination of ligands by the metal cation.[6]

While the above does reflect a harmonic development of a branch of science from the classical to the molecular approach, in nonaqueous solvents a strange state of affairs exists. Indeed, modern kineticists and spectroscopists have often applied their techniques to solutions of, say, transition metal ions in nonaqueous solvents.[7] However, the corresponding classical measurements like thermodynamical and transport ones are often lacking (perhaps due to the decline of electrochemistry in the current fashion list of scientific topics).

Still, the classical measurements are needed since they often give necessary and precise information like the degree of association and the activity of an electrolyte. It is enough to think of the dangers of neglecting association in arriving at any conclusion about the rate of exchange of the solvent around a particular cation.

If the anion that one must necessarily add participates in the first and even the second coordination sphere as a complexed or paired species,[7] the rate of exchange of the solvent can be dramatically altered. This may happen both because of a statistical effect of occupation of an exchange site or because the partial or total charge neutralization may effect the tightness by which the solvent is retained in the coordination shell around the metal cation.[8]

In an effort to avert the present situation and to rebalance our state of knowledge of the classical and nonclassical information of divalent ions in nonaqueous solvents, it has been decided in this laboratory to carry measurements of electrical conductance of Mg^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} *m*-benzendisulfonates in methanol. The choice of the anion has been dictated by a parallel study by P-jump relaxation kinetics[9] and by the solubility ($\sim 5 \times 10^{-2}$ *M*) being high enough to carry a conductance study without difficulties. Methanol has been chosen as the natural starting point from water. The conductance of K_2BDS has also been measured in order to calculate the limiting conductance of the benzenedisulfonate anion in methanol.

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