LEWIS ACID–BASE TITRATION EMPLOYING MEGACYCLE-FREQUENCY OSCILLATORS

PART I. TITRATIONS INVOLVING ALUMINUM CHLORIDE IN ACETONITRILE SOLUTION

ELDON T. HITCHCOCK* AND PHILIP J. ELVING

University of Michigan, Ann Arbor, Michigan (U.S.A.)

Investigators concerned with the study of the mechanism and stoichiometry of chemical reactions are constantly on the alert for new and more penetrating means of detecting and following the course of chemical reactions. In particular, the analytical chemist is interested in improved methods for equivalence-point detection in titrimetry.

Since the relatively recent introduction of megacycle-frequency ("high frequency") oscillator circuits[1-5], their applicability has been described, *e.g.* for end-point indication in titration in aqueous and nonaqueous solvents, analysis of binary systems, and measurement of reaction rates. While the megacycle-frequency titration curves may, in some cases, resemble conventional low-frequency, *e.g.* 1000-cycle, conductance curves, two important differences distinguish the former technique:

(*a*) lack of contact between electrodes and test solution, and

(*b*) the possibility of instrument response to solution conductance, solution dielectric constant, or both.

The theory of the electronic circuitry involved in megacycle-frequency oscillometry, developed by REILLEY AND McCURDY[5,6], relates the instrument response to the low-frequency conductance of the solution, the dielectric constants of cell walls and solution, and the oscillator frequency. For the instrument used in the present studies, which employs a capacitance coupled cell, it is possible to compensate for the cell wall capacitance by introducing the proper amount of series inductance; when solution conductance is negligible, the instrument response then varies linearly with solution capacitance and therefore with solution dielectric constant. This permits following reactions which may only involve coordinate bond formation, *e.g.* molecular association and hydrogen bonding. When such reactions are followed by a megacycle-frequency oscillator, they may be considered *capacimetric titrations.*

The foregoing suggests the application of megacycle-frequency titrimetry to the study of Lewis acid–base reactions, since available means for following such titrations are few and are often cumbersome or lacking in sensitivity[7].

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* Present address; Colorado College, Colorado Springs, Colorado (U.S.A.).

Titration of Lewis acids and bases

The general concepts of acids and bases, and the role of the solvent have been ably summarized by BELL[8] and KOLTHOFF[7]. Acid–base equilibria and titration in non-aqueous solvents have been reviewed by KOLTHOFF AND BRUCKENSTEIN[9] and FRITZ[10].

Because of the basic character of water toward molecular Lewis acids, reactions between Lewis acids and bases cannot be generally studied in aqueous media. The choice of solvent is further limited by the fact that solvents containing oxygen or nitrogen also react with Lewis acids to varying degrees. Reactions between Lewis acids and very weak bases must be performed in inert solvents for the intended reaction to proceed to "completion" without interfering solvent competition.

Numerous qualitative studies of molecular Lewis acid–base reactions (*e.g.* refs.[11–14]) have attempted to demonstrate the acidic and basic properties of the compounds involved and to establish a relative acidity scale. The nature of the addition complexes formed has been studied by various techniques, *e.g.*, spectrophotometry[15], thermo-metry[16,17], phase diagrams[18] and dielectric data[19,20].

While vapor phase reactions, usually involving elaborate vacuum line equipment, have been carried out, little has been reported regarding the application of titrimetric techniques to the quantitative study of Lewis acid–base reactions in solution. Limitations on such titrations stem from the inherent nature of the reactions: difficulty in equivalence-point detection; limited solvents available; necessity of using high-purity solvents and of excluding atmospheric moisture and carbon dioxide; possible dimerization, association or ion-pair formation involving reactants and/or reaction products in solvents of low dielectric constant[21].

Few color indicators are available[22]. Physical methods used to follow the titrations have included conductometry[23–27], potentiometry[24], thermometry[28,29], cryoscopy[30] and photometry[31]. Several nitrogen bases have been titrated with boron trifluoride in dioxane using a megacycle-frequency oscillator[32]; bases weaker than pyridine could not be titrated.

Base strength studies

Information on the relative base strengths of Lewis bases is of importance for several reasons, *e.g.*, in predicting which of two donor functional groups will react preferentially with a given Lewis acid, in rate control of certain Lewis acid-catalyzed reactions, and in explaining the large changes in reaction rates which frequently result when the solvent is changed[33]. The methods used to obtain such data are varied, *e.g.*, effect of oxygen bases in deactivating the acid catalyst in a given reaction[33], shift in the O-D infrared absorption band of methanol-d in the presence of excess base[34], and molar heats of mixing[35,36]. NMR spectra are a means of judging the relative electron density around the donor atom in the molecule[37]. Stability constants for addition complexes determined by, for example, spectrophotometry[38] and manometry[39] provide a direct measure of the base strength of the donor molecule with respect to the acceptor molecule.

Objectives of the present studies

In the light of the unique response of megacycle-frequency oscillators especially to reactions occurring in solvents of low dielectric constant, it was decided to apply this

technique to following the reactions between two typical Lewis acids, aluminum chloride and stannic chloride, and a variety of bases consisting of various organic nitrogen and oxygen compounds in a moderately reactive solvent, acetonitrile (dielectric constant 36) and in a relatively inert solvent, benzene (dielectric constant 2.3).

The objectives of the investigation were threefold. The successful use of the oscillators for end-point determination in protonic acid–base titration in nonaqueous solvent encouraged extension of the technique to the titration of Lewis acids and bases. The second objective involved interpretation of the characteristic shapes of the titration curves obtained. Third, it was desirable to evaluate the usefulness of the megacycle-frequency titration data as a measure of the relative base strength of Lewis bases toward a given Lewis acid.

The present paper presents the studies involving aluminum chloride; a second paper[40] will present those involving stannic chloride; a third[41] will describe the isolation and identification of adducts predicted by the titration curves.

TITRATIONS INVOLVING ALUMINUM CHLORIDE

Because of its generally high acid strength[42], aluminum chloride was investigated as a Lewis acid in acetonitrile as solvent. While a comparative study of its reaction with Lewis bases in an inert solvent such as benzene or carbon tetrachloride would have been helpful, the extremely low solubility of aluminum chloride in the latter solvents prohibited their use.

Structure of aluminum chloride

By analogy to BF_3, uncomplexed monomeric aluminum chloride would be expected to have a coplanar trigonal configuration. Coordination with a fourth group would. change this to a tetrahedral one. In pure aluminum chloride, the tetrahedral configuration is attained through formation of the dimer, Al_2Cl_6. This double tetrahedral configuration, first suggested by FAJANS[43], is supported by X-ray and electron diffraction studies, which have shown the liquid and vapor states of aluminum chloride to be very similar in structure[44,45]. The latter is also supported by the normal Trouton constant of aluminum chloride. The ionic bonding scheme of the crystalline structure[46] is indicated by the relatively high melting point, large heat of fusion, and high electrical conductivity of solid aluminum chloride. The sharp decrease in conductivity, which occurs as the compound melts, supports conversion to a covalent bonding structure in the liquid state.
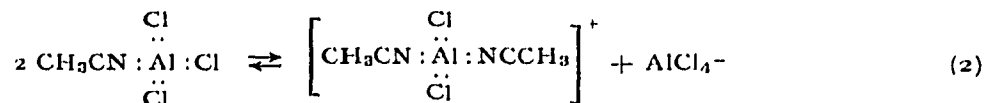
Aluminum chloride in solution

Aluminum chloride exists predominately as the dimer in "inert" solvents; however, evidence exists for some dissociation in benzene at mole fractions less than 0.001[47]:

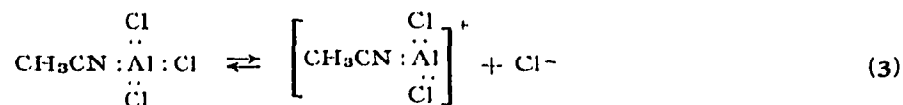$$Al_2Cl_6 \rightleftharpoons 2 \; AlCl_3 \tag{1}$$

On the other hand, when the dimer is dissolved in a solvent whose molecules have electron donor properties stronger than those of the chlorine atom, the bridged chlorines are displaced by the stronger base, opening the dimer and producing monomeric solvated aluminum chloride[48].

In the present study, a negligible solubility was found for aluminum chloride in benzene at 25°; the oscillator response to the reaction of bases with a benzene solution saturated with aluminum chloride was so small that titration was impossible. In addition, aluminum chloride apparently reacted slowly but continuously with benzene; the solution acquired a deepening green coloration with time, indicating a constantly changing composition. Toluene and carbon tetrachloride gave similar difficulties so that the attempt to use these solvents for aluminum chloride was abandoned.

Acetonitrile, being basic and therefore a good solvent for aluminum chloride[49], was satisfactory; standard solutions prepared in it were stable. Aluminum chloride would be expected to exist in this solvent in a monomeric form complexed with solvent molecules. The relatively large dielectric constant of acetonitrile (36) would favor partial dissociation of the complex into ions, thus accounting for the observed electrical conductivity. The ionization is probably

$$2\ CH_3CN : \overset{\overset{\displaystyle Cl}{\cdot\cdot}}{\underset{\underset{\displaystyle Cl}{\cdot\cdot}}{Al}} : Cl \quad \rightleftharpoons \quad \left[CH_3CN : \overset{\overset{\displaystyle Cl}{\cdot\cdot}}{\underset{\underset{\displaystyle Cl}{\cdot\cdot}}{Al}} : NCCH_3 \right]^{+} + AlCl_4^{-} \tag{2}$$

rather than simply

$$CH_3CN : \overset{\overset{\displaystyle Cl}{\cdot\cdot}}{\underset{\underset{\displaystyle Cl}{\cdot\cdot}}{Al}} : Cl \quad \rightleftharpoons \quad \left[CH_3CN : \overset{\overset{\displaystyle Cl}{\cdot\cdot}}{\underset{\underset{\displaystyle Cl}{\cdot\cdot}}{Al}} \right]^{+} + Cl^{-} \tag{3}$$

Reasons for believing eqn. (2) to represent the ionization are: (a) aluminum thus maintains a coordination number of 4 (its most stable configuration), and (b) aluminum chloride gives a van 't Hoff factor of unity in another basic solvent (nitrobenzene) of almost identical dielectric constant[26]. Further association of acetonitrile molecules with aluminum chloride is shown by the isolation of the adduct $AlCl_3 \cdot 2CH_3CN$ from aluminum chloride solutions in acetonitrile[41].

Megacycle-frequency titrations involving nitrogen bases

Table I summarizes the titration of a series of nitrogen bases with aluminum chloride, in which acid was added to base and base to acid in the concentration range of 10^{-2} to 10^{-3} M. The molar ratios given in the final column were calculated from the end-points as read from the curves by conventional extrapolation. Typical titration curves are shown in Figs. 1 and 2.

Curves for the titration of bases (Fig. 1A) are characterized by an initial positive slope, whose magnitude depends on the base being titrated, followed by an arm of greater positive slope. From the start of the titration a white flocculant precipitate forms, likely from the reaction

$$2\ base + AlCl_3(solvent)_n \rightarrow AlCl_3 \cdot 2\ base + n\ solvent \tag{4}$$
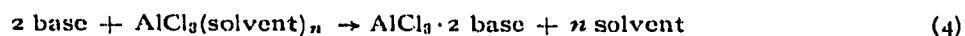
The reaction is completed at the point where the slope of the curve sharply increases; beyond this point, the excess aluminum chloride causes all of the curves to have the form of the $AlCl_3$ concentration response curve (Fig. 3). The shape of the latter, which is of the same general shape as that for an electrolyte in aqueous solution, is

explicable on the basis that aluminum chloride is solvated by the basic solvent and undergoes partial dissociation into ionic species.

Reaction 4 is essentially the displacement of coordinated solvent molecules by the stronger nitrogen bases, giving insoluble products. The formation of other multiple base complexes is likely[50] during the first part of the titration, but these are evidently very weakly associated compared to the AB_2 complex.

TABLE I

TITRATION OF NITROGEN BASES WITH ALUMINUM CHLORIDE IN ACETONITRILE

Base present or used (mmoles)	Approx. cell concn. (mM)	AlCl₃ used or present (mmoles)	Titration ratio base: acid	Base present or used (mmoles)	Approx. cell concn. (mM)	AlCl₃ used or present (mmoles)	Titration ratio base: acid
Pyridine				p-Toluidine			
0.223	2.2	0.103	2.16	0.210	2.1	0.1035	2.03
0.446	4.5	0.189	2.36	0.526	5.3	0.240	2.19
0.557	5.6	0.234	2.38	1.052	10.5	0.402	2.63
0.557	5.6	0.238	2.34	0.118a	1.2	0.0527	2.24c
1.115	11.1	0.425	2.62	0.234a	2.3	0.1057	2.22c
0.1037	1.0a	0.0527	1.97c	0.336a	3.3	0.1585	2.12c
0.207	2.1a	0.1057	1.97c				
0.310	3.1a	0.1585	1.96c	Dimethylaniline			
0.441	4.4a	0.211	2.09c	0.514	5.1	0.232	2.22
0.1135	1.1a,b	0.0527	2.15c	0.721	7.2	0.277	2.60
0.228	2.3a,b	0.1057	2.16c	1.029	10.3	0.422	2.44
0.228a,b	2.3	0.1057	2.16c	0.1029a,b	1.0	0.0527	1.97f
0.345a,b	3.4	0.1585	2.18c	0.1029a,b	1.0	0.0527	1.97f
				0.2068a,b	2.1	0.1057	1.96f
Quinoline				0.340a,b	3.4	0.1585	2.14f
0.205	2.0	0.097	2.12				
0.513	5.1	0.228	2.25	Diphenylguanidine			
0.718	7.2	0.314	2.29	0.5035	5.0	0.209	2.40
1.026	10.3	0.445	2.31	1.007	10.0	0.412	2.50
0.1129a	1.1	0.0527	2.14d	1.510	15.1	0.610	2.48
0.209a	2.1	0.1057	1.98d	0.404a	4.0	0.211	1.91
0.305a	3.0	0.1585	1.93d				
0.2093a,b	2.1	0.1057	1.98d	Tri-n-butylamine			
				0.118a	1.2	0.0527	2.24g
				0.225a	2.2	0.1057	2.13g
				0.336a,b	3.4	0.1585	2.13g

a These experiments involve titration with AlCl₃ in the cell and the base used as the titrant.
b In these experiments sufficient base to exceed formation of the 1 : 1 complex was added and only the latter portion of the titration curve was measured.
c Average of this group = 2.08 ± 0.08.
d Average of set = 2.01 ± 0.07.
e Average of set = 2.19 ± 0.05.
f Average of set = 2.01 ± 0.06.
g Average of set = 2.17 ± 0.05.

The extent of deviation from an exact AB_2 ratio at the extrapolated end-point increases with increased concentration (cf. Table 1), probably owing to adsorption of excess base by the flocculant precipitate. The latter is quite voluminous when the concentration approaches 10^{-2} M.

Curves for the reverse-order titration (addition of base solution to aluminum

solution) are all of similar general shape, being characterized by a maximum in the general vicinity of a $1:1$ molar ratio followed by a decrease, which levels off at close to an AB_2 ratio (Fig. 1B). The latter ratios are the ones recorded in Table I. An AB_2 stoichiometry is more nearly attained when the base is added to $AlCl_3$ than when $AlCl_3$ is added to base.
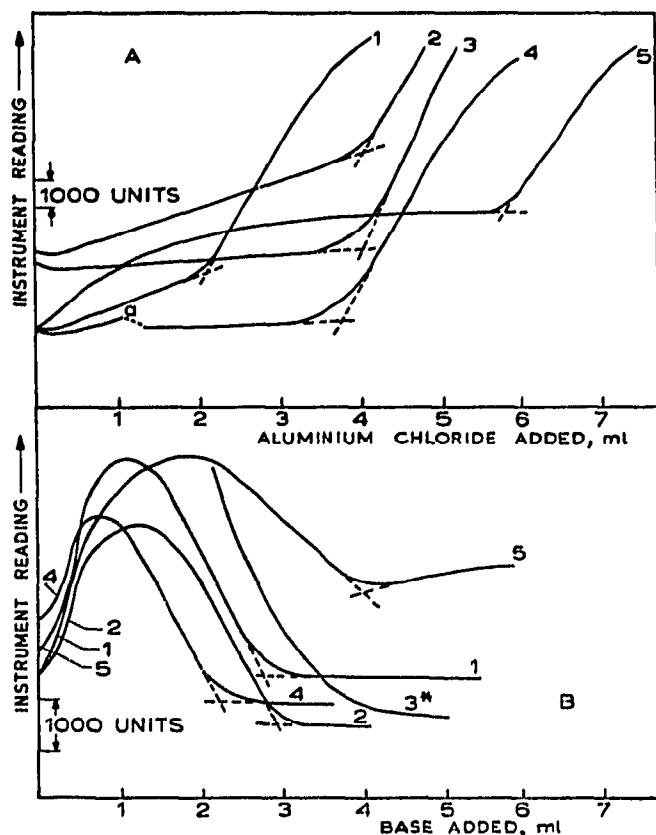

Fig. 1. Representative titration curves (solvent: acetonitrile; compensator setting: o). (A) Titration of 100 ml of nitrogen base solution with 0.1057 M AlCl$_3$. (1) 0.56 mmole pyridine present; (2) 1.03 mmole quinoline; (3) 1.03 mmole dimethylaniline; (4) 1.05 mmole p-toluidine; (5) 1.5 mmole diphenylguanidine. At point a on curve 4, precipitate began to form; in all other titrations precipitate formed from the beginning. (B) Titration of 100 ml of aluminum chloride solution with approximately 0.1 M nitrogen base. (1) 0.1585 mmole AlCl$_3$ with pyridine; (2) 0.1588 mmole AlCl$_3$ with quinoline; (3) 0.1585 mmole AlCl$_3$ with dimethylaniline; (4) 0.1057 mmole AlCl$_3$ with p-toluidine; (5) 0.211 mmole AlCl$_3$ with diphenylguanidine; (3*) same as 3 but sufficient base added in first increment to exceed $1:1$ molar ratio.
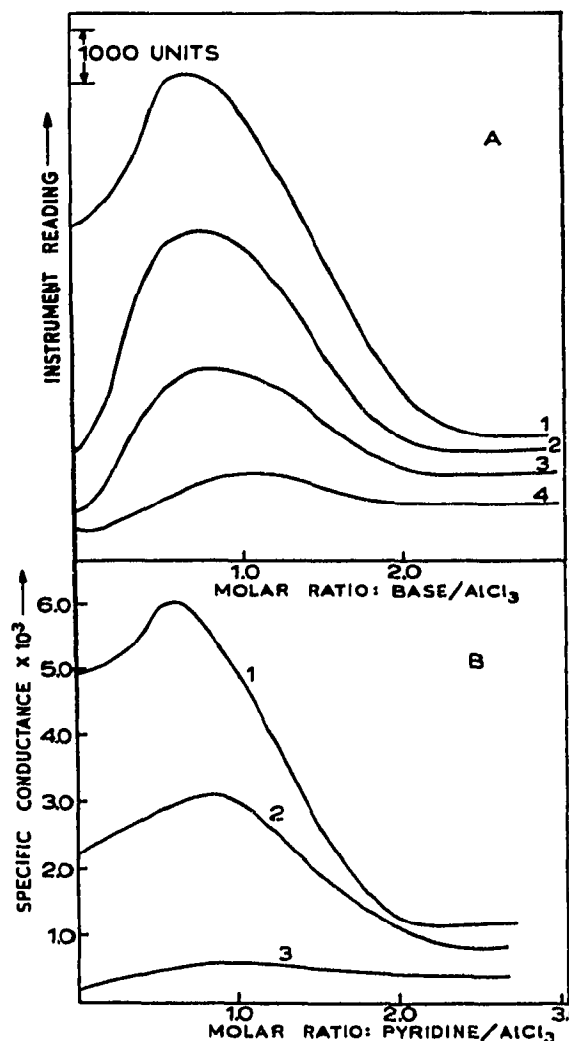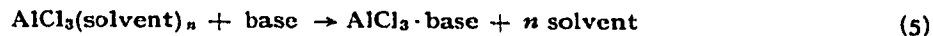

Fig. 2. Titration of aluminum chloride solutions in acetonitrile with pyridine solution in acetonitrile. (A) Megacycle-frequency titration of 100 ml of aluminum chloride solution with 0.1115 M pyridine (compensator setting: o). (1) 0.00211 M AlCl$_3$; (2) 0.00158 M AlCl$_3$; (3) 0.00106 M AlCl$_3$; (4) 0.000527 M AlCl$_3$. (B) Conductometric titration of 50 ml of aluminum chloride solution with 0.100 M pyridine (1) 0.0077 M AlCl$_3$; (2) 0.0035 M AlCl$_3$; (3) 0.0007 M AlCl$_3$.

Since very little precipitate appears before the maximum is reached, it seems logical to assume that, during the ascent to the maximum, the reaction is

$$AlCl_3(solvent)_n + base \rightarrow AlCl_3 \cdot base + n \; solvent \tag{5}$$

where the $1:1$ complex undergoes greater ionization than the complex of aluminum chloride with the solvent (cf. previous discussion). Addition of base beyond the AB ratio forms the insoluble AB_2 complex, which precipitates as a white floc,

$$AlCl_3 \cdot base + base \rightarrow AlCl_3 \cdot 2 \; base \tag{6}$$
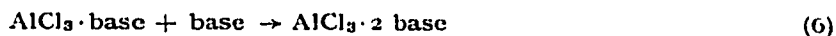
Removal of the $1:1$ complex from solution explains the negative slope which follows the maximum. At the lower plateau, all of the AB complex has been converted into the insoluble AB_2 species, and further addition of base has little or no effect on the instrument response.
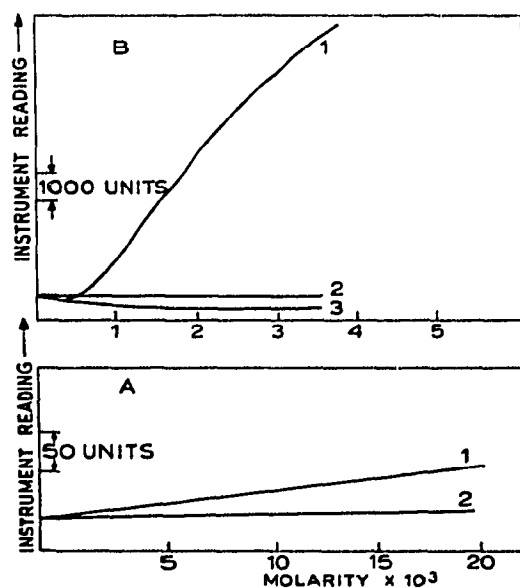

Fig. 3. Oscillator–concentration response curves (the instrument response scale varies for the different items). (A) Benzene solution: (1) stannic chloride and (2) ethyl ether at compensator setting of 1500. (B) Acetonitrile solution: (1) aluminum chloride, (2) pyridine and (3) stannic chloride at compensator setting of 0.

Several titrations were run by adding enough base in the first increment to pass the maximum point in the curve. Readings were then taken, from which extrapolation gave the end-point for formation of the AB_2 adduct. Much time was saved by this procedure at no evident sacrifice of precision. These titrations are suitably marked in Table I and Fig. 1B.

The effect of concentration on the apparent stoichiometry is seen by plotting oscillator response vs. molar ratio of base: acid (Fig. 2A). With increasing concentration, the maximum shifts to lower values, while the second equivalence point shifts slightly to higher values. The first shift is likely due to formation of some insoluble AB_2 adduct before all of the $AlCl_3$ has formed the AB adduct, which would result in a decrease in instrument response before the $1:1$ molar ratio is reached. The

second shift is possibly caused by adsorption of added base on the flocculant pre-cipitate (AB₂ adduct) before all of the AB adduct is converted into the AB₂ adduct.

The behavior of three bases of different strength and type is compared in Fig. 4. Diphenylamine apparently forms only a weak 1:1 complex with aluminum chloride in acetonitrile, since the curve levels off at this ratio and no precipitate appears. Although there is only a small difference between the basic strengths in water of
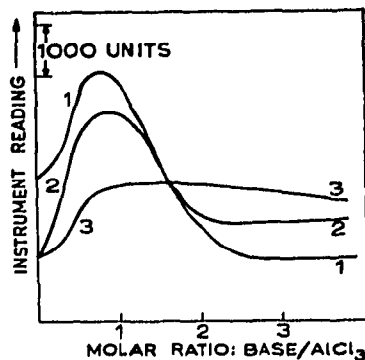

Fig. 4. Difference in oscillator response on the addition of approximately 0.1 M nitrogen base solution to 100 ml of acetonitrile containing 0.1057 mmole AlCl₃ (compensator setting: 0). (1) p-toluidine; (2) pyridine; (3) diphenylamine.

p-toluidine, a typical aromatic amine (pK_b = 8.70), and pyridine, a typical hetero-cyclic nitrogen base (pK_b = 8.85), a significant difference is indicated in their activity toward aluminum chloride in acetonitrile. At the 1:1 molar ratio the p-toluidine reaction with aluminum chloride produces greater ionic concentration than the pyridine reaction; at the AB₂ ratio, p-toluidine precipitates the ionic species from solution more completely than does pyridine.

Low-frequency conductance

For comparison, aluminum chloride was titrated with pyridine, using a conventional 1000-cycle conductance bridge. The titration curves (Fig. 2B) are generally similar to the megacycle-frequency ones for the same reaction (Fig. 2A). The curve maximum shifts similarly with increased concentration. No conclusion can be drawn regarding a shift in the second equivalence point, since a good extrapolation could be made only in the case of the most concentrated aluminum chloride solution.

The similarity of the curves supports the conclusion that conductivity plays a major role in the megacycle-frequency response to the aluminum chloride–pyridine reaction in acetonitrile in the concentration range used. The range of low-frequency conductance in this titration evidently falls on the initial positive slope portion of the megacycle-frequency conductance curve[5,6] so that a simple linear relationship exists between the two types of conductance.

Titrations involving oxygen bases

Titrations involving aluminum chloride and oxygen bases in acetonitrile proved unsatisfactory due either to negligible instrument response to reactions involving alcohols and ethers or to unsteady instrument readings in the case of water.

DISCUSSION

Addition of Lewis bases, which are stronger than acetonitrile, to solutions of aluminum chloride in acetonitrile causes a displacement of coordinated solvent; the new complex formed may ionize. The conductivities observed on addition of oxygen and nitrogen bases to solutions of aluminum chloride in nitrobenzene have been explained as due to the differing degrees of ionization of the complexes formed[26]. Conductance measurements made in the present study indicate that the ionic dissociation of the aluminum chloride–pyridine adduct in acetonitrile is greater than that of the aluminum chloride–solvent adduct (cf. Fig. 2B).

Although the titration curves of Figs. 1 to 3 bear a formal resemblance to those observed by BRYANT AND WARDROP[51] for the 1000-cycle conductometric titration of organic acids and tertiary nitrogen bases in acetone and acetonitrile, the phenomena causing them are different. The maxima in the present studies occur at a molar ratio of 1:1; those in the Bryant–Wardrop study occur when equivalent amounts of acid and salt are present, i.e. at the half-neutralization of the acid, and are ascribed to the formation of hydrogen-bonded species between acid and anion, which show enhanced dissociation into free ions.

In a review of Friedel-Crafts complexes[16], ELEY states that only 1:1 complexes of aluminum chloride with oxygen and nitrogen bases have been isolated except in the case of ammonia where a greater degree of complexation seems to be possible. Others have reported the formation of multiligand complexes of aluminum chloride with pyridine, although the most stable is the 1:1 species (cf. ref.[52]).

In the present investigation, the megacycle-frequency titration curves clearly indicate the conversion of the AB complex into a AB_2 complex in the reaction of six different nitrogen bases with aluminum chloride in acetonitrile. Low-frequency conductance titration of aluminum chloride with pyridine in acetonitrile also indicates formation of an AB_2 complex. This is in agreement with the conductance titrations of VAN DYKE et al.[26,27], who reported formation of multiple complexes for aluminum halides with nitrogen and oxygen bases in nitrobenzene and benzonitrile. Titration of aluminum chloride with Lewis bases in thionyl chloride, selenium oxychloride and other solvents has been reviewed[7].

An initial minimum frequently occurs in the instrument response curves obtained on successive addition of a compound to the solvent, as well as in some titration curves. Since this minimum appears only when the solvent is water, acetic acid or acetonitrile, but not benzene, it must be associated with ionic equilibria occurring in the better ionizing solvents and is a phenomenon arising from the conductance rather than the capacitance of the solution. A similar minimum is often noted in conventional low-frequency titration curves.

Precision and reproducibility

Besides the usual titrimetric and curve extrapolation errors, a slight fluctuation in instrument reading contributed to the total error in the megacycle-frequency titrations; this was due to the stability characteristics of the resonating circuit and to the possible absorption of moisture from the atmosphere during the titration. However, since these were long-term fluctuations and a given titration could usually be completed in less than 5 or 10 min, their effect on the shape of the titration curve and the final extrapolated end-point was negligible. The energy of the circuit is too

small to produce heat effects with time[53]; the concentrations used (0.003 M or less) were too low to give any significant temperature increase during reaction.

While the stoichiometry of the Lewis acid–base reactions, as indicated by the titration curves, was not clear in every case, good reproducibility was achieved for all titrations and response curves. Experimental variables such as rate of stirring, small temperature fluctuations (less than $5°$) and small time intervals between addition of titrant and reading of instrument had no effect on reproducibility. However, titrations in acetonitrile required an appreciable time to reach constant instrument reading, especially when an adduct was being precipitated. Zero adjustment of the instrument was often necessary at the beginning of a titration in order to correct for small differences in instrument reading owing to different positions of the titration cell in the cell holder and the inherent long-term fluctuation of the oscillator circuit. The magnitude of this adjustment amounted to less than 1% of the instrument reading in most cases.

CONCLUSIONS

The present investigation has demonstrated the usefulness of megacycle-frequency oscillators in studying Lewis acid–base reactions. The method is convenient, rapid and sensitive, requiring no elaborate setup or time-consuming operations. Commercially available equipment can be used. In titrations involving electrical conductance, the megacycle-frequency technique appears to be more rapid and more sensitive than the conventional conductometric titration technique.

The Lewis acid, aluminum chloride, has been successfully titrated with nitrogen bases in acetonitrile as solvent with an error in accuracy ranging from 0.5 to 4 % for the different bases used; reverse order titrations were equally successful. While this accuracy does not approach that which is possible in conventional protonic acid–base titrations, it does compare favorably with other titrimetric techniques available for Lewis acid–base reactions. The particular advantage of the megacycle-frequency technique over the latter is the speed with which the titration can be performed.

From the positions of the maxima, minima and other inflection points in the titration curves, conclusions can be drawn regarding the stoichiometry of the reactions occurring during the progressive addition of base to acid or of acid to base.

EXPERIMENTAL

Chemicals

Acetonitrile (Eastman Kodak yellow label) was purified[54] by shaking with cold, saturated potassium hydroxide solution, drying over anhydrous sodium carbonate, and distilling from phosphorus pentoxide through an 18-inch Fenske column; the distillate (0.5° range) was free of detectable moisture (Karl Fischer reagent). Reagent-grade benzene (Baker and Adamson), after standing over anhydrous calcium sulfate for several hours, was similarly distilled. Contact of the solvents with atmospheric moisture was minimized.

Nitrogen, used as a flushing gas for the megacycle-frequency titration cell, was dried and brought to vapor pressure equilibrium with the solvent being used by successive passage through concentrated sulfuric acid, anhydrous calcium sulfate and anhydrous solvent.

All other chemicals were either reagent grade or Eastman Kodak white label quality.

Standard solutions

Aluminum chloride, 0.1 M in acetonitrile, prepared by rapidly transferring the salt into the solvent, was stored in automatic microburets and standardized by either the Volhard method or potentiometric titration of the chloride with silver nitrate.

Approximately 0.1 M solutions of the following reagent-grade bases were prepared in acetonitrile: pyridine, quinoline, p-toluidine, dimethylaniline, diphenylguanidine, tri-n-butylamine, diphenylamine and indole. These solutions were standardized by pipetting a 2.0-ml aliquot into a 125-ml Erlenmeyer flask, adding 25 ml of glacial acetic acid, two drops of methyl violet indicator (0.2 g/100 ml chlorobenzene), and titrating with standard perchloric acid in glacial acetic acid.

Apparatus

Automatic 5-ml microburets were equipped with anhydrous calcium sulfate drying tubes; silicone stopcock grease was used on ground-glass joints.

A Leeds and Northrup No. 7664 pH meter was used for potentiometric titration with silver nitrate with Ag/AgCl and glass electrodes as indicating and reference electrodes, respectively.

Conductometric titrations were performed using a Serfass line-operated, 1000-cps conductivity bridge (Arthur H. Thomas Model RCM15) and a closed, calibrated conductance cell.

Megacycle-frequency oscillator

The megacycle-frequency measurements were made with the Model V Oscillometer (E. H. Sargent), which has a resonant frequency of about 5 mc and operates on the circuit retune principle, in which the resonating tank circuit containing the capacitive-coupled titration cell is brought back into resonance after each change in composition of the cell contents by adjusting a variable capacitor in parallel with the titration cell. Dial units corresponding to this parallel capacitance constitute the instrument reading.

The instrument response is primarily due to the equivalent capacitance of the cell contents and can be made linear to the latter's dielectric constant for solutions of low dielectric constant and negligible conductance by introducing into the cell circuit in series a variable inductor, whose reactance may be adjusted to equal the capacitive reactance due to the cell walls. Under these conditions, the instrument reading is directly proportional to the capacitive reactance of the cell contents and therefore to the dielectric constant of the solution. The variable inductor (E. H. Sargent) is calibrated in arbitrary units from 0 to 3000 and is referred to in this paper as the cell compensator.

The linearity obtained upon introducing series inductance is accompanied by a large increase in sensitivity, but is limited to the dielectric constant range of 0 to 20. A compensator setting of 1500 was used for measurement in benzene; no compensation was used for titration in acetonitrile, since the increased sensitivity throws the instrument response off-scale for solvents with high dielectric constants.

The titration cell (Fig. 5) was modified from the one furnished with the cell holder, H (E. H. Sargent). Two cell caps, constructed for the purpose of excluding moisture, provided for insertion of buret, stirrer, and flushing-gas inlet and exit. For titrations
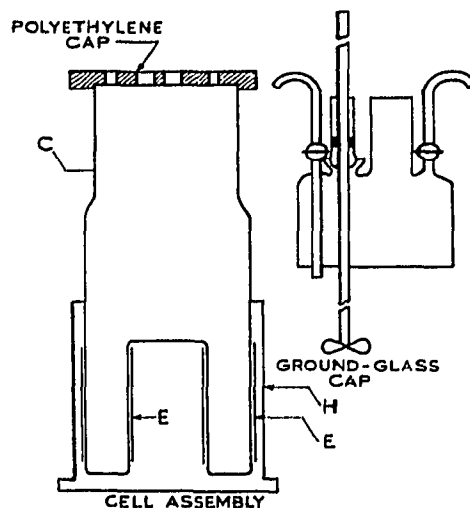

Fig. 5. Cell assembly. C is the oscillometer cell (capacity of *ca.* 150 ml) inserted into the cell holder, H. The electrodes, E, are concentric metal bands sealed to the outside of the glass cell walls.

involving aluminum chloride and stannic chloride in acetonitrile, a polyethylene cap was used. For titrations in benzene, a fitted ground-glass cap was used along with a cell having a ground-glass joint at the mouth.

Oscillator titration procedure

Approximately 100 ml of solvent were placed in the dry megacycle-frequency titration cell, bringing the liquid level to about 1 cm above the electrodes. An aliquot of base solution was rapidly added to the cell, the polyethylene cap quickly put into place, the flushing gas (nitrogen) (50 ml/min) and stirrer started, and titration begun. For the reverse titration, an aliquot of Lewis acid solution was added to 100 ml of solvent in the cell; 0.1 M base solution was added from a 5.0-ml microburet. Operations preceding actual titration were performed as rapidly as possible to avoid contact with atmospheric moisture. The use of titrant increments of 0.1 or 0.2 ml gave titration curves with 15 to 30 plotted points. After each addition, time was allowed for the instrument response to reach stability before the reading was taken; this amounted to a few seconds or several minutes, depending on the concentration and stage in the titration (more time was required at higher concentrations and in the vicinity of a change in titration curve slope). Least time was required midway on any of the straight-line portions of the titration curve. Corrections for dilution were unnecessary because of the small volume of titrant added.

Conductometric titration procedure

First, 50 ml of acetonitrile was added to the cell; then, a known volume of standard aluminum chloride solution. The cap was quickly put in place, and the flushing gas

and magnetic stirrer were started. After the initial conductance reading, standard pyridine solution in acetonitrile was added through the fitted ground-glass cap in increments of 0.1 to 0.4 ml; readings were taken after each addition.

Instrument response curves

These were obtained by procedures similar to the titration procedures except that the compounds were added to pure solvent in the titration cell.

SUMMARY

An investigation of the applicability of megacycle-frequency oscillators to following reactions between Lewis acids and bases was initiated with the following objectives: (*1*) quantitative determination of Lewis acids and bases by titration, (*2*) evaluation of reaction stoichiometry, and (*3*) measurement of relative base strength of Lewis bases with respect to a given Lewis acid.

The Lewis acid, aluminum chloride, has been titrated with nitrogen bases in acetonitrile as solvent with an accuracy of 0.5 to 4%, which compares favorably with that attainable by other techniques for following Lewis acid–base reactions. The method is convenient, rapid and sensitive; commercially available equipment can be used. In titrations involving electrical conductance, the megacycle-frequency technique appears to be more rapid and more sensitive than conventional conductometry.

The shapes of the titration curves (positions of inflection) give information regarding the species forming during the course of reaction. It was thus shown that aluminum chloride forms soluble AB adducts and insoluble AB₂ adducts in acetonitrile with pyridine, quinoline, *p*-toluidine, dimethylaniline, diphenylguanidine and tri-*n*-butylamine; diphenylamine forms only a soluble AB adduct. The relative degree of ionization of the various adducts, including that of aluminum chloride with the solvent, can be estimated.

RÉSUMÉ

Les auteurs ont effectué une étude sur les possibilités d'application des oscillateurs à haute fréquence (mégacycle) pour suivre les réactions des acides et bases de Lewis. L'acide de Lewis, chlorure d'aluminium, a été titré par des bases azotées, dans l'acétonitrile comme solvant. La méthode est satisfaisante, plus rapide et plus sensible que la conductométrie conventionnelle.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die Anwendungsmöglichkeit eines Hochfrequenz-Oscillators zum Studium der Reaktionen zwischen Lewis-Säure (Aluminiumchlorid) und organischen Basen. Das beschriebene Verfahren ist schneller und empfindlicher als die konduktometrische Methode.

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