Fifteen ml. of 1.5 molar benzoyl chloride in dioxide and 5 ml. of pyridine were transferred to each of two 250-ml. volumetric flasks. Five ml. of a dioxane solution, containing 8.6 millimoles of acetamide, was added. The mixtures were heated together with blanks for one hour at 70°. At the end of this time the samples were cooled. Anhydrous methanol was added to both samples in two increments—first, 2 ml. and after five minutes 23 ml. To one 10 ml. of pyridine was added and the final solution titrated with 0.5 *N* aqueous sodium hydroxide. The other was titrated directly with 0.5 *N* sodium methylate in methanol.

In the first case any anhydride formed would hydrolyze to two moles of free acid, but in the anhydrous environment the anhydride would titrate mole for mole with the methylate

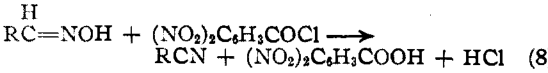
$$(C_6H_5CO)_2O + NaOCH_3 \longrightarrow C_6H_5COOCH_3 + C_6H_5COONa \quad (7)$$

Thus the net result would be low in proportion to the amount of anhydride formed. Results of 60 and 62%, respectively, indicated that little or no anhydride was formed under these conditions.

It is interesting to note that acetamide and 3,5-dinitrobenzoyl chloride showed no evidence of benzoylation. An experiment in which excess reagent was decomposed with water gave 0.0% reaction.

No interference was encountered from N-substituted amides, urethans and anilides. Negative results were obtained on urethan, amyl carbamate, melamine, dimethylformamide, acetanilide and propionanilide. Obviously amines or alcohols will not interfere beyond using up some of the reagent.

Interfering Substances.—Water and free acids interfere by increasing the hydrogen ion concentration of the final solution. Since both reactions are stoichiometric, however, the results can be corrected directly. Aldoximes presumably are dehydrated according to the reaction



$$R\overset{H}{C}{=}NOH + (NO_2)_2C_6H_3COCl \longrightarrow RCN + (NO_2)_2C_6H_3COOH + HCl \quad (8)$$

An experiment in which butyraldoxime was heated at 60° for thirty minutes with the acyl chloride gave an increase in acidity equivalent to 89% dehydration.

The authors extend their thanks to L. B. Woolaver, of this laboratory, for his aid in the identification of the adipamide reaction product and in the analysis of several of the amides.

Summary

1. A new procedure for the determination of primary amides, based on quantitative reaction with 3,5-dinitrobenzoyl chloride, has been described.

2. Quantitative analytical data are presented for sixteen amides. The variable reactions of several other amides are discussed.

3. The reactions of acetamide with other acylating agents have been examined.

4. The subject of interfering substances is discussed briefly.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL UNIVERSITY]

Donor-Acceptor Bonding. III. Methyl Cyanide Addition Compounds of Boron Trichloride and Boron Trifluoride

BY A. W. LAUBENGAYER AND D. S. SEARS[1]

The conditions favoring the formation of molecular addition compounds by donor–acceptor bonding and the important consequences of such bonding have been discussed in the first paper of this series.[2] The cyanide group with an unshared pair of electrons on the nitrogen has strong donor possibilities and many 1:1 addition compounds of cyanides with acceptor molecules, such as the boron halides, have been reported. Since the data available on such compounds have been very limited, the present comprehensive investigation of $CH_3CN:BCl_3$ and $CH_3CN:BF_3$ has been carried out. These systems are well suited for equilibrium studies over a considerable temperature range. $CH_3CN:BF_3$ has been described briefly by Patein[3] and by Bowlus and Nieuwland.[4]

In $CH_3CN:BCl_3$ and $CH_3CN:BF_3$, the boron atoms have tetrahedral coördination and the carbon, nitrogen and boron atoms should have a linear arrangement, giving symmetrical molecules favorable for structural studies. Because they are virtually completely dissociated in the vapor phase it has been impossible to determine their structures by electron diffraction methods, but a study of their crystal structures by X-ray diffraction methods will be undertaken.

Experimental

Preparation.—The compound $CH_3CN:BCl_3$ was prepared by allowing methyl cyanide to distill slowly *in vacuo* into liquid boron trichloride at −70°. The reaction vessel was attached to a vacuum apparatus[5] and any excess of reactant was removed by distillation. The compound was transferred in an anhydrous atmosphere to a

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[1] Present address: The B. F. Goodrich Co., Akron, Ohio.

[2] Laubengayer and Finlay, THIS JOURNAL, **65**, 884 (1943).

[3] Patein, *Compt. rend.*, **113**, 84 (1891).

[4] Bowlus and Nieuwland, THIS JOURNAL, **53**, 3835 (1931).

[5] Laubengayer and Corey, *J. Phys. Chem.*, **30**, 1043 (1926).

vacuum sublimator[6] and was purified by sublimation at 85°. Well-formed crystals collected on the cold finger and these were transferred in a dry atmosphere to a weighing bottle.

$CH_3CN:BF_3$ was prepared by bubbling boron trifluoride gas directly into liquid methyl cyanide contained in a flask protected from atmospheric moisture by a drying tube. The crystalline product so obtained was quickly washed free of excess methyl cyanide with anhydrous benzene on a Buchner funnel and was then purified by vacuum sublimation at room temperature.

The solid compounds obtained in this manner were colorless crystals which fumed in moist air due to hydrolysis, but they could be stored without decomposition in glass-stoppered weighing bottles kept over phosphorus pentoxide.

Analysis.—Samples for analysis were prepared by a process of double sublimation *in vacuo* into small ampules which were sealed off. Aqueous solutions were obtained by breaking these ampules in glass-stoppered Erlenmeyer flasks. Chlorine was determined by precipitation as silver chloride. Boron was determined by decomposing the sample by alkaline hydrolysis, followed by differential titration with hydrochloric acid and sodium hydroxide, using mannitol. Nitrogen was determined by hydrolyzing the compound with 1:4 sulfuric acid in a sealed tube at 100°. The solution prepared in this way contained ammonium sulfate and the nitrogen was removed as ammonia in a semi-micro Kjeldahl apparatus.

Anal. Calcd. for $CH_3CN:BCl_3$: Cl, 67.21; N, 8.8. Found: Cl, 67.27, 67.19; N, 8.7. Calcd. for $CH_3CN:BF_3$: B, 9.9; N, 12.9. Found: B, 10.1, 9.4; N, 12.6, 12.9.

Melting Points and Densities.—Small amounts of these materials were sublimed into melting point tubes and sealed off under vacuum. $CH_3CN:BCl_3$ melted with decomposition at 195–200° and $CH_3CN:BF_3$ melted at 135.5 ± 0.5°. Patein[3] reported that $CH_3CN:BF_3$ melted at 120°, while Bowlus and Nieuwland reported that it melted at 87° and boiled at 101° (752 mm.). We believe that our data are more accurate because of the high purity of the samples secured by vacuum sublimation.

The densities $d^{20°}_{4°}$ of solid $CH_3CN:BCl_3$ and $CH_3CN:BF_3$, determined by immersion in saturated solutions of benzene or toluene in a vacuum pycnometer, were 1.603 ± 0.005 and 1.59 ± 0.05°, respectively.

Optical Examination.—Microscopic examination of these compounds was rendered very difficult because of their reactivity toward water and some of the common immersion media. Examination of the crystals formed in sample tubes during sublimation and also of crystals immersed in paraffin oil showed that both compounds belong in the orthorhombic system. Biaxial interference figures were obtained and all principal views showed parallel extinction. The crystals were rather highly birefringent.

Saturation Vapor Pressure Measurements.—These were made for both compounds with an isotensiscope[5] having a volume of 15 cc., using samples of about 1 g. $CH_3CN:BCl_3$ was studied in the range 50 to 160° and $CH_3CN:BF_3$ from 20 to 110°, readings being taken at about eight degree intervals. The heating curves were retraced on cooling, demonstrating that equilibrium had been attained and that no irreversible secondary decomposition had occurred. The equations $\log_{10} P$ mm. = $(-3646/T) + 11.3040$ for $CH_3CN:BCl_3$ and $\log_{10} P$ mm. = $(-2896/T) + 10.5794$ for $CH_3CN:BF_3$ summarize the data, the mean percentage deviation of calculated from observed pressures being about 1%.

Vapor Densities and Heats of Dissociation.—Vapor density measurements were made on samples of these compounds which were completely vaporized, as ascertained by direct observation. The measurements in the upper temperature regions were made in an all-glass cell employing a "sickle" pressure gage.[7] Further measurements were made at lower temperatures using a modified Dumas bulb. This consisted of a liter bulb connected to a side chamber by means of small bore tubing. After introducing the sample into the side chamber and evacuating highly on a mercury pump the bulb was sealed off. The whole assembly was immersed in a thermostated bath and allowed to come to equilibrium. The side chamber was then sealed off from the main bulb, and the pressures employed in the calculations were taken from the isotensiscopic curves. The data are given in Tables I and II.

TABLE I

DISSOCIATION DATA FOR $CH_3CN:BCl_3$

	Temp., °C. ± 0.1	Press., mm. ± 0.1	Degree of dissocn.
Sample No. 1, 0.2100 g. in 719 cc, sickle cell	132.1	93.0	0.996
	140.0	94.6	.992
	143.7	95.1	.985
	144.6	96.0	.999
	150.1	97.4	1.002
Sample No. 2, 0.0644 g. in 233.3 cc. sickle cell	123.7	86.4	1.000
	130.0	87.7	0.999
	146.5	91.3	.999
Sample No. 3, 0.2054 g. in 233.5 cc. sickle cell	148.8	290.5	.985
	160.3	299.1	.990
	164.9	302.6	1.01^{7}
Sample No. 4, 0.1197 g. in 1113.8 cc. Dumas bulb	99.0	31.5	0.998

TABLE II

DISSOCIATION DATA FOR $CH_3CN:BF_3$

	Temp., °C. ± 0.1	Press., mm. ± 0.1	Degree of dissocn.
Sample No. 1, 0.2270 g. in 234 cc. sickle cell	99.7	409.1	0.978
	103.3	413.2	0.978
Sample No. 2, 0.1099 g. in 1117 cc. Dumas bulb	49.8	36.5	1.003

From these data it is apparent that the dissociation of these compounds is virtually complete in the vapor phase in the temperature and vapor concentration ranges studied. This fact has been further substantiated for the compound $CH_3CN:BCl_3$. An electron-diffraction study[8] was made of this compound in the gas phase at 95° and the results were in complete agreement with the idea that the vapor consists only of a mixture of methyl cyanide and boron trichloride.

The fact that these compounds are completely dissociated in the vapor phase permits an evaluation of the equilibrium constant, K_p, as a function of temperature, directly from the isotensiscopic data. For the dissociation of solid to

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(6) The vacuum sublimator was somewhat similar to that described by L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., New York, N. Y., 1941, 2nd ed., Pt. II, p. 299.

(7) Laubengayer and Schirmer, THIS JOURNAL, 62, 1578 (1940).

(8) We are indebted to Professor S. H. Bauer of this laboratory for help with this phase of the investigation. Electron diffraction patterns were obtained for the vapor in equilibrium with solid $CH_3CN:BCl_3$ (vapor tension, 30 mm.). A radial distribution curve was computed and was found to agree excellently with the "synthetic" radial distribution curve for an equi-molar mixture of methyl cyanide and boron trichloride. A comparison of the observed intensity pattern with the theoretical intensity curve, computed on the assumption of complete dissociation, also gave good agreement. This quantitative agreement between the observed and computed peak positions was so good that we can cite our data as confirming the previous structure determinations of methyl cyanide and boron trichloride: see L. Pauling, H. D. Springall and J. K. Palmer, THIS JOURNAL, 61, 927 (1939); H. A. Levy and L. O. Brockway, *ibid.*, 59, 2085 (1937).

gaseous components, $K_p = P_{\text{total}}^2/4$. Expressing K_p in terms of atmospheres and substituting in the vapor pressure equations gives the equations $\log K_{p(\text{atm.})} = (-7292/T) + 16.2444$ for $CH_3CN:BCl_3$ and $\log K_{p(\text{atm.})} = (-5792/T) + 14.7951$ for $CH_3CN:BF_3$. From these the heats of dissociation of the solid molecular compounds to the gaseous components are calculated to be 34.4 and 26.5 kcal., respectively.

It is noteworthy that in the course of the vapor density studies on the two systems the completely vaporized and dissociated samples showed an exceedingly great tendency to undercool. When condensation was realized the associated crystalline phase was always found as a single crystal formed at one point in the cell.

Calorimetric Studies and Heats of Formation.—Calorimetric measurements were made in a Bunsen ice-calorimeter such as that described by Hieber and Mühlbauer.[9] The cell fitted into a four-liter Dewar cylinder which was packed with crushed ice and surrounded with felt to minimize heat transfer. The heats of solution for all substances, with the exception of boron trifluoride, were determined by breaking small ampules in about 20 cc. of water. During the course of a run the liquid was stirred mechanically. Corrections were made for the heat of stirring and for the heat leak of the system. The heat of solution of boron trifluoride had been determined[2] by adding the gas to the reaction vessel through a capillary jet from a mercury gas buret.

The heats of vaporization of boron trichloride and methyl cyanide at 0° were calculated from data obtained from the literature.[10] The thermal data are summarized in Table III. The values 33.8 and 26.5 kcal. for the heats of formation of $CH_3CN:BCl_3$(s) and $CH_3CN:BF_3$(s), respectively, from the gaseous components check very well with the values derived for the heats of dissociation from vapor pressure data. This check substantiates the conclusion, reached on the basis of the vapor density data, that the addition compounds are completely dissociated in the vapor phase.

It is not possible to interpret the over-all heats of formation in terms of the energy of the donor-acceptor bond, since the heats of sublimation of the addition compounds are unknown and because of other contributing terms which are unknown. However, the relative values of the above results are seen to be reasonable if we assume that the crystal energies of the two compounds are of the same order of magnitude. We should expect less heat to be evolved in the formation of $CH_3CN:BF_3$ than for $CH_3CN:BCl_3$ because more energy should be required to distort the boron trifluoride molecule to a tetrahedral configuration than to bring about a similar change in boron trichloride.

TABLE III

	ΔH in kcal.
HEATS OF SOLUTION AT 0°	
BCl_3(l) in water	65.1 ± 0.2
BF_3(g) in water	21.9 ± .2
CH_3CN(l) in water	1.1 ± .2
$CH_3CN:BCl_3$(s) in water	44.9 ± .3
$CH_3CN:BF_3$(s) in water	4.5 ± .3
HEATS OF VAPORIZATION AT 0°	
BCl_3	4.5
CH_3CN	8.0
HEATS OF FORMATION	
$CH_3CN:BCl_3$(s) from CH_3CN(g) and BCl_3(g)	33.8 ± 0.3
$CH_3CN:BF_3$(s) from CH_3CN(g) and BF_3(g)	26.5 ± .3

Molecular Weight Determinations of CH_3CN: BF_3 in Benzene.—$CH_3CN:BF_3$, although more soluble than $CH_3CN:BCl_3$, is relatively insoluble in benzene and dissolves to the extent of only about 0.34 g. per 100 g. of benzene at 25°. Cryoscopic measurements on this compound were made in benzene in a cell especially constructed for vacuum work. At molalities of 0.0118, 0.0184 and 0.0234 the molecular weight was found to be 115, 128, 115 ± 5, respectively. The agreement with the calculated molecular weight 109 is about as good as can be expected in view of the large error due to the low concentrations of the solutions available. The results indicate that in dilute solutions in benzene the molecular species $CH_3CN:BF_3$ does exist and is not appreciably dissociated.

Dipole Moment Measurements on CH_3CN: BF_3.—The apparatus used in making these measurements was a heterodyne oscillator operating at a frequency of 1.54 megacycles. The dipole cell, having a capacitance of about 55.2 cm., was of the type described by Smyth.[11]

The solutions were prepared by subliming $CH_3CN:BF_3$ *in vacuo* into a bulb and then distilling very pure benzene onto the sample. These solutions were transferred to the dipole cell without coming in contact with air. The measurements were made at 25 ± 0.05° and the results are listed in Table IV.

TABLE IV

DIPOLE MOMENT OF $CH_3CN:BF_3$ IN BENZENE AT 25°

f_2	ϵ	d	P_2	$P_{\text{orientation}}$	μ
Benzene					
	2.274	0.8725			
$CH_3CN:BF_3$					
0.001036	2.298	0.8730	395		
.001101	2.302	.8732	412		
.002189	2.384	.8734	757	712	5.8 ± 0.2
.002329	2.382	.8735	700		

The anomalous trend of the molar polarization values must be attributed to experimental difficulties. The range of concentration was very

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(9) Hieber and Mühlbauer, *Z. anorg. allgem. Chem.*, **186**, 97 (1930).

(10) "International Critical Tables," McGraw-Hill Book Co., Inc., New York, N. Y., 1929, 1st ed., p. 136.

(11) Smyth, THIS JOURNAL, **50**, 1547 (1928).

limited due to the low solubility of the compound. The value for the dipole moment is calculated from an average of the two highest values and, although the selection of these values is not completely justified, the result is probably a close approximation to the true dipole moment.

The high polarity found for $CH_3CN:BF_3$ is consistent with the postulate that the fluorine atoms occupy tetrahedral coördination positions about the boron, with a linear configuration of the carbon, nitrogen and boron atoms. In such a structure there should be large contributions all in the same direction by the $C\equiv N$, N–B and B–F bonds.

Because of the inappreciable solubility of $CH_3CN:BCl_3$ in benzene and other non-polar solvents we were unable to find suitable conditions for measuring its moment. This insolubility in non-polar solvents is strong indication of high polarity for the compound. Ulich and Nespital[12] reported a dipole moment of 7.65 debyes for $CH_3CN:BCl_3$. They gave no data except the final value and did not mention their experimental method so that it is impossible to form an opinion of the accuracy of their figure.

Summary

1. The compounds $CH_3CN:BCl_3$ and $CH_3CN:BF_3$ have been prepared and their properties listed.

2. Saturation vapor pressure measurements have been made. Vapor density measurements lead to the conclusion that the dissociation of these compounds in the vapor phase is virtually complete. From these measurements the heats of dissociation of $CH_3CN:BCl_3(s)$ and $CH_3CN:BF_3(s)$ to the gaseous components are found to be 33.4 and 26.5 kcal., respectively.

3. Heats of formation of $CH_3CN:BCl_3(s)$ and $CH_3CN:BF_3(s)$ from the gaseous components have been determined calorimetrically as 33.8 and 26.5 kcal.

4. Molecular weight determinations made cryoscopically in benzene indicate that the molecule $CH_3CN:BF_3$ exists and is not appreciably dissociated in dilute solutions.

5. Dipole moment measurements on $CH_3CN:BF_3$ indicate that the dipole moment is approximately 5.8 debyes.

ITHACA, NEW YORK RECEIVED JUNE 1, 1944

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[12] Ulich and Nespital, *Z. angew. Chem.*, **44**, 752 (1931).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF TEXAS]

Spectrophotometric Studies on Cerium(IV) Sulfate Complex Ions

BY ROBERT LEE MOORE AND ROBBIN C. ANDERSON

There is much evidence for the existence of complex ions in aqueous solutions of cerium(IV) sulfate. This includes observations of transference,[1] electromotive force measurements,[2,3,4] kinetic studies,[5] and the existence of double salts and so-called "cerate" compounds such as $(NH_4)_2Ce(NO_3)_6$,[4] but there is little experimental evidence concerning the actual nature of these complex ions.

In the past several years, the spectrophotometer has been used to study a number of complex ions which show characteristic colors.[6,7,8] Since in general the addition of sulfate to solutions of ceric salts causes readily visible color changes, spectrophotometric studies of cerium(IV) sulfate solutions were undertaken in an attempt to obtain evidence concerning the nature of the complex ions responsible for these color changes.

Experimental

Materials

Cerium(IV) Sulfate Solutions.—These were prepared and standardized by the methods previously described.[5] Ordinary "C. P." cerium(IV) oxide was carefully purified by precipitation of the basic nitrate, and dissolved by digestion with sulfuric acid and dilution with water. The total cerium content was determined by titration with iron(II) ammonium sulfate and the acidity by removing the cerium with oxalate and then titrating with base.

Cerium(IV) Perchlorate Solutions.—These were prepared by a method essentially the same as that described by Smith[9] and Sherrill.[10] Specially purified cerium(IV) oxide was dissolved in sulfuric acid. Cerium(III) oxalate was precipitated and washed free of sulfate. The oxalate was dissolved in nitric acid and the resulting solution digested first with hydrochloric acid and then with perchloric acid to convert to cerium(III) perchlorate. This was oxidized electrolytically, about 97% conversion usually being obtained. The solutions were stored in the dark and standardized just before use by the same methods as used for the cerium(IV) sulfate solutions.

Perchloric Acid.—Solutions were prepared from Baker C. P. 60% perchloric acid and distilled water.

Sodium Sulfate and Sodium Perchlorate.—Solutions of C. P. reagent grade sulfuric acid and perchloric acid were carefully standardized against sodium hydroxide solution. Salt solutions of the desired concentration were then prepared by mixing equivalent quantities of acid and base.

Apparatus and Procedure.—The instrument used was a Beckman Quartz Photoelectric Spectrophotometer[11] covering a range from 200 to 2000 mμ. The wave length scale is accurate to better than 1 mμ and the light transmission measurements are accurate within about 0.2% under the conditions used in this investigation.

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[1] Jones and Soper, *J. Chem. Soc.*, 805 (1935).

[2] Kuntz, THIS JOURNAL, **53**, 98 (1931).

[3] Noyes and Garner, *ibid.*, **58**, 1265 (1936).

[4] Smith and Getz, *Ind. Eng. Chem., Anal. Ed.*, **10**, 191 (1938).

[5] J. W. Moore and R. C. Anderson, THIS JOURNAL, **66**, 1476 (1944).

[6] Bent and French, *ibid.*, **63**, 568 (1941).

[7] Vosburgh and Cooper, *ibid.*, **63**, 437 (1941).

[8] Rabinowitch and Stockmayer, *ibid.*, **64**, 291 (1942).

[9] Smith, "Cerate Oxidimetry," G. Frederick Smith Chem. Co., Columbus, Ohio, 1942, p. 5.

[10] Sherrill, King and Spooner, THIS JOURNAL, **65**, 170 (1943).

[11] Carey and Beckman, *J. Optical Soc. Am.*, **31**, 682 (1941).