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The boron trifluoride nitromethane adduct

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Abstract

The separation of the boron isotopes using boron trifluoride · organic-donor, Lewis acid · base adducts is an essential first step in preparing ^{10}B enriched and depleted crystalline solids so vital to nuclear studies and reactor applications such as enriched MgB_2, boron carbide, ZrB_2, HfB_2, aluminum boron alloys, and depleted silicon circuits for radiation hardening and neutron diffraction crystal structure studies. The appearance of this new adduct with such superior properties demands attention in the continuing search for more effective and efficient means of separation. An evaluation of the boron trifluoride nitromethane adduct, its thermodynamic and physical properties related to large-scale isotopic separation is presented. Its remarkably high separation factor was confirmed to be higher than the expected theoretical value. However, the reportedly high acid/donor ratio was proven to be an order of magnitude lower. On-going research is determining the crystal structure of deuterated and ^{11}B enriched $^{11}BF_3 \cdot CD_3NO_2$ by X-ray and neutron diffraction.

Keywords: Boron; Isotope; Separation; BF_3 · nitromethane adduct; Lewis acid–base complex

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1. Introduction

The separation of the boron isotopes is accomplished by gas–liquid exchange reactions [1] of the type.

$$^{10}BX_{3(g)} + {}^{11}BX_3 \cdot \text{donor}_{(l)} = {}^{11}BX_{3(g)} + {}^{10}BX_3 \cdot \text{donor}_{(l)}, \tag{1}$$

where X = H, CH_3, or a halogen and the $BX_3 \cdot \text{donor}_{(l)}$ is a Lewis acid · base complex or adduct.

The equilibrium constant, K_{eq}, for reaction (1) is

$$K_{eq} = \frac{[^{11}BX_{3(g)}][^{10}BX_3 \cdot \text{donor}_{(l)}]}{[^{10}BX_{3(g)}][^{11}BX_3 \cdot \text{donor}_{(l)}]} = \frac{[^{10}B/^{11}B]_{(l)}}{[^{10}B/^{11}B]_{(g)}}. \tag{2}$$

In order to efficiently separate the isotopes, the following four criteria must be considered.

1. K_{eq} must be maximized to minimize the number of stages necessary for a given enrichment.
2. Equilibrium must be established rapidly for a high throughput in a continuous system.
3. BX_3 must be readily liberated from the donor for recirculation (adduct formation reaction thermally reversible).
4. Adduct must be sufficiently stable to not decompose into unwanted reaction products Based on the excellent electron acceptor capabilities of BF_3 and the first and fourth criteria, all studies have used X = F. Furthermore, all studies using BCl_3 have shown that the K_{eq}'s were lower than those using the BF_3 Lewis acid. Therefore the isotopic exchange reaction may be rewritten as:

$$^{10}BF_{3(g)} + {}^{11}BF_3 \cdot \text{donor}_{(l)} = {}^{11}BF_{3(g)} + {}^{10}BF_3 \cdot \text{donor}_{(l)}. \tag{3}$$

Although BF_3 is the most powerful electron acceptor (Lewis acid) known, the number of atomic species capable of donating electrons to BF_3 is relatively small. Only nine elements, H, N, O, F, P, S, Cl, Se, and Te, in some of their compounds are capable of donating electrons to BF_3. In particular, oxygen donors [2–9], sulfur donors [2,3,5–7,9–11], nitrogen and other donors [3,5–9] have been studied.

The separation of the boron isotopes using boron trifluoride · organic-donor, Lewis acid · base adducts is an essential first step in preparing ^{10}B enriched applications, including boron carbide control rods, ZrB_2, HfB_2, neutron absorbers, aluminum boron alloy spent fuel casks, superconductivity mechanism

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determination in MgB_2 (isotope effect), radiation hardening (shielding), boric acid chemical shim, boron carbide control rods) or ^{10}B depleted applications (neutron diffraction structural studies, controlled doping by ion implantation (bit flop), single event transient, neutron induced upsets, radiation hardening in silicon circuits.

1.1. Historical background and the $BF_3 \cdot$ nitromethane adduct

Prior to 1943, only mass spectroscopy and thermal diffusion were used for separation of the boron isotopes [12]. During the Manhattan project, Lewis acid · donor complexes were used. Many adducts were studied concentrating on the oxygen and sulfur containing donors. The project culminated in the choice of the $BF_3 \cdot$DME adduct for the first US production plant [13].

This work was kept secret during WW II and was not declassified until 1957 and published from 1958 into the early 1960s by Palko et al. and others [2–11,14,15].

Most of the isotopic separation adducts studied showed BF_3/donor ratios of 1.00 ± 0.16 so that an equal number of moles of acceptor and donor could be assumed for most calculations without appreciable error. The exception to this rule was found in the $BF_3 \cdot$nitrobenzene adduct which had a ratio <0.05.

Literature on the $BF_3 \cdot$nitromethane adduct began to appear in the early 1990s. It was first described as a superior catalyst for cyclization reactions [16–19]. From 1992 to 1994 its use in preparing annulations [20–22] of trienoate and of (±)-taxodione was published based on Harring's 1992 Ph.D. dissertation from the University of Minnesota [16]. It has also been shown to be a remarkably efficient catalyst in the creation of stereospecifically pure enantiomers [23–25] and opening ring structures allowing substitutions or creating linear compounds [26–33].

About the same time it was also suggested as a much more cost effective and efficient means of separating the isotopes of boron. Herbst and McCandless studied several ketones and nitromethane as possible replacement donors for dimethyl ether [1]. Each of those studied had greater separation factors than the $\alpha = 1.027$ for the $BF_3 \cdot$DME. They concluded that each of these could significantly reduce the isotope separation plant size if they replaced the DME donor.

1.2. Theoretical maximum K_{eq}

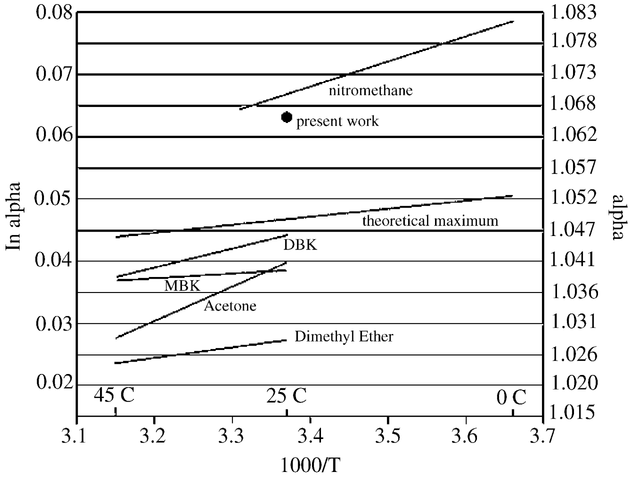

Fig. 1. Separation coefficient vs. $1/T$ after Herbst [1].

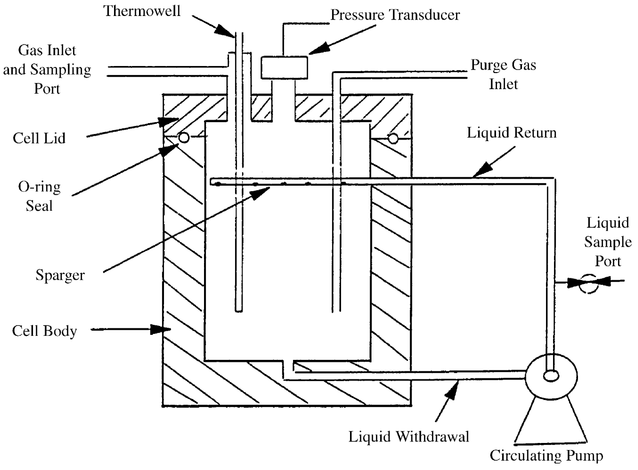

Fig. 2. Schematic of equilibrium cell to measure isotopic equilibrium after Herbst [1].

Statistical thermodynamics vibrational partition functions and spectroscopic data provide the theoretical basis for estimating the maximum K_{eq} of any $BF_3 \cdot$ donor adduct [1]. At 303 and 250 K the maximum K_{eq} corresponds to 1.047 and 1.056, respectively. Linear extrapolation gives:

$$\ln K_{eq} = \ln \alpha = 12.23/T(\mathrm{K}) + 0.00556, \tag{4}$$

$$\text{where } \alpha \text{ (the separation factor)} = \frac{[^{10}B/^{11}B]_{(l)}}{[^{10}B/^{11}B]_{(g)}}. \tag{5}$$

Herbst and McCandless showed [1] that whereas the three new ketone donors approached the theoretical maximum more closely than $BF_3 \cdot$DME, the $BF_3 \cdot CH_3NO_2$ significantly exceeded it! (see Fig. 1). They postulated that this unique feature could be the result of the two oxygen atoms providing the necessary electron pairs yielding two donor sites for nitromethane compared to a single donor site for the other donors.

They stated [1] that "It is conceivable that excess BF_3 dissolved in the liquid (*donor*) phase beyond that mandated by a 1:1 molar complex could be associated with or weakly bound to the second oxygen… and could potentially result in larger values of α than for …single site donors." Harring reported to Herbst, privately, that the BF_3/CH_3NO_2 ratio was between 1.4/1 and 1.6/1 supporting the two donor site idea. Herbst stated that "These properties were confirmed in this laboratory…" [15].

Because of the very long standing reliance on some of the first adducts to be used in the separation of the boron isotopes, the appearance of this new adduct with such superior properties demands attention in the continuing search for more effective and efficient means of separation.

1.3. *Potential promise of* $BF_3 \cdot CH_3NO_2$

The much higher separation factor, α, (≈ 1.06 vs. 1.03) would require about half the number of theoretical plates making the required separation column much shorter. The much higher BF_3/donor ratio (≈ 1.6 vs. 1.1) would mean that the diameter of the required column could be much smaller. These two factors would make the capital expense much less.

2. Experimental

All experiments were conducted in a dry box [34] maintaining a water vapor content $\leqslant 20$ ppm. The adduct was made by reacting BF_3 gas with nitromethane in a custom-made stainless-steel cell following the design of Herbst [35]. Nitromethane was re-circulated with a Teflon peristaltic pump to a sparger port at the top of the cell to allow maximum liquid–gas contact (see Fig. 2). The cell could be heated or cooled via copper cooling coils welded to the cell.

2.1. *Density*

Volumetric vials, precise to 0.01 mL filled with the adduct, were weighed on a digital balance, precise to 0.001 g. Density of water previously measured by this method was accurate to ± 0.003 g/cm^3. Three separate measurements of the adduct density yielded an average density of 1.31 g/cm^3 which is 15% greater than that of pure nitromethane (1.137 g/cm^3).

2.2. *Thermal stability*

The adduct, when heated in the dry box, exhibited dissociation with BF_3 bubble formation around the thermometer and beaker glass surfaces at 40°C in increasing amounts to 65°C where it stopped. No more bubbles formed until 100.8°C (nitromethane b.p.) was reached. Therefore, isotopically enriched BF_3 can easily be separated from this donor at 65°C allowing for reclamation and recirculation of the donor in an isotopic separation plant.

2.3. *Re-measuring the* BF_3/CH_3NO_2 *ratio*

The ratio is necessary to determine the heat of association which is key to understanding what makes this adduct so effective as a catalyst and an isotopic separator. This ratio is also important because it determines the size of the gas–liquid contact equipment in an isotopic separation plant which is inversely related to the concentration of boron in the complex. Any gain in the reduction of the column length due to the increased α could be negated by the increased column diameter due to a decreased boron content in the adduct.

2.4. BF_3/CH_3NO_2 *ratio by titration at UMR*

Nitromethane (−29°C m.p.) was pressurized with 120,000 Pa BF_3 and cooled to −40°C overnight [35]. It did not freeze, indicating complete conversion to the adduct (−49°C m.p.). One milliliter of this adduct was diluted in 30 mL nitromethane. A measured sample of the mixture was then mixed with 100 mL distilled water forming a weak HF. The acid was then titrated with NaOH.

2.5. BF_3/CH_3NO_2 *ratio by gravimetric analysis*

The weighed cell was half-filled with nitromethane, re-weighed and frozen, 4000 Pa evacuated at −60°C, returned to STP, then pressurized with BF_3 to 240,000 Pa overnight. The adduct was frozen to −90°C (−49°C m.p.), evacuated, and sealed to remove $BF_{3(g)}$ before being brought back to STP and weighed so that the BF_3/CH_3NO_2 ratio could be calculated.

2.6. BF_3/CH_3NO_2 *ratio by titration at EP*

The second total boron titration was done at the Eagle Picher Boron Labs by ASTM C-791 & C-809. This technique consists of dissolving the adduct in water, titrating with NaOH to the neutral inflection point, adding excess manitol producing mannitoboric acid which was then titrated to the second end-point allowing the boron content to be calculated.

2.7. *Heat of association*

The heat of association was measured in a Tronac Model 450 Isoperibol Titration Calorimeter by breaking glass ampules of $BF_3 \cdot CH_3NO_2$, diethyl ether, and $BF_3 \cdot$diethyl ether underneath a large quantity of nitromethane.

2.8. *Isotopic separation factor,* α

To compare with published data the α was determined by injecting the liquid and gas phase separately into an

HP Model 5988 Mass Spectrometer from equilibrated glass vials containing the adduct.

3. Results and discussion

3.1. BF_3/CH_3NO_2 ratio results

The two titration methods and the gravimetric method all produced the same result, which was an order of magnitude smaller than the published result of 1.6/1 and much smaller than the more usual 1/1 ratio. The ratio was found to be 0.158/1 by all three methods. The remarkable properties of this new adduct cannot be explained by a higher BF_3/donor ratio than other adducts.

3.2. Heat of association

Once this ratio, n, was established, it was possible to calculate the heat of association as shown:

$$\begin{aligned}&(C_2H_5)_2O\cdot BF_{3(l)} + (100+1/n)(CH_3NO_2)_{(l)}\\&\quad = (1/n)[(BF_3)_n\cdot CH_3NO_2]_{(NM)}\\&\qquad + (C_2H_5)_2O_{(NM)} + 100(CH_3NO_2)_{(l)},\end{aligned} \tag{6}$$

where n is the BF_3 / nitromethane ratio, and (NM) refers to a nitromethane solution. For this reaction,

$$\Delta H_1 = +0.73\ \text{kJ/mol}.$$

$$\begin{aligned}&(C_2H_5)_2O_{(l)} + 100(CH_3NO_2)_{(l)}\\&\quad = (C_2H_5)_2O_{(NM)} + 100(CH_3NO_2)_{(l)},\\&\Delta H_2 = +3.86\ \text{kJ/mol},\end{aligned} \tag{7}$$

$$\begin{aligned}&[(BF_3)_n\cdot CH_3NO_2]_{(l)} + 100(CH_3NO)_{(l)}\\&\quad = [(BF_3)_n\cdot CH_3NO_2]_{(NM)}\\&\qquad + 100(CH_3NO_2)_{(l)},\\&\Delta H_3 = -3.56[1+0.5262(n-1)]\ \text{kJ/mol}.\end{aligned} \tag{8}$$

These equations can be combined to give

$$\begin{aligned}&n[(C_2H_5)_2O\cdot BF_{3(l)}] + CH_3NO_{2(l)}\\&\quad = [(BF_3)_n\cdot CH_3NO_2]_{(l)} + n(C_2H_5)_2O_{(l)},\\&\Delta H_4 = n(\Delta H_1 - \Delta H_2) - \Delta H_3.\end{aligned} \tag{9}$$

Filling in the measured quantities: $\Delta H_4 = -1.26n + 1.69$ kJ/mol.

Also, ΔH_4 can be written as

$$\begin{aligned}\Delta H_4 = {}&\Delta H_f[(BF_3)_n\cdot CH_3NO_2]\\&+ n\Delta H_f[(C_2H_5)_2O_{(l)}]\\&- n\Delta H_f[(C_2H_5)_2O\cdot BF_{3(l)}]\\&- \Delta H_f[CH_3NO_{2(l)}]\end{aligned}$$

which can be rearranged to show

$$\begin{aligned}\Delta H_f[(BF_3)_n\cdot CH_3NO_2]_{(l)} &= \Delta H_4 - n\Delta H_f[(C_2H_5)_2O_{(l)}]\\&\quad + n\Delta H_f[(C_2H_5)_2O\cdot BF_{3(l)}] + \Delta H_f[CH_3NO_{2(l)}].\end{aligned}$$

Again, filling in known quantities:

$$\begin{aligned}&\Delta H_f[(BF_3)_n\cdot CH_3NO_2]_{(l)}\\&\quad = \Delta H_4 - 1202.8n - 113.1\ \text{kJ/mol}.\end{aligned}$$

The heat of association can now be written, using the values found above and known values,

$$\begin{aligned}\Delta H_{\text{assoc}} = {}&\Delta H_f[(BF_3)_n\cdot CH_3NO_2]_{(l)}\\&- \Delta H_f[CH_3NO_{2(l)}] - n\Delta H_f[BF_{3(g)}]\\= {}&-1.26n + 1.69 - 1202.8n - 113.1\\&- (-113.1) - n(-1137.0)\ \text{kJ/mol}.\end{aligned}$$

Using the ratio found in this study, $n = 0.158$, this gives a heat of association of -8.51 kJ/mol BF_3. The specific heat of the adduct was measured at the same time as the heats of reaction, and was found to be 0.34 ± 0.01 J/g°C in the range 0–23°C.

3.3. Isotopic separation factor, α

The $^{10}B/^{11}B$ ratio determined $\alpha = 1.060$, agreeing with Herbst and McCandless [1] ($\alpha = 1.066$).

4. Conclusion

The BF_3/CH_3NO_2 ratio was only 10% of the value reported in the literature. This requires that the column diameter and related packing costs be much higher than with the traditional Anisole or DME donors. Although the high α was confirmed and would decrease the column height, the potential danger of using nitromethane did not offset the cost advantage. The remarkable properties of this new adduct cannot be explained by a higher BF_3/donor ratio than other adducts.

5. Future work

The very low BF_3/CH_3NO_2 ratio begs the question of the bonding between the donor and acceptor. It was decided to freeze the adduct as described previously and determine its crystal structure by X-ray and neutron diffraction. In order to see the hydrogen positions, deuterated nitromethane has been acquired. Since boron-10 atoms absorb thermal neutrons, Eagle Picher, LLC will donate a lecture bottle of $^{11}BF_3$ and $^{11}BF_3\cdot CD_3NO_2$ will be used for the crystal structure determination.

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