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# Vibrational spectra and relative stabilities of the van der Waals complexes of boron trifluoride with *cis*-2-butene, *trans*-2-butene and 2-methyl propene<sup>☆</sup>

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## Abstract

The mid-infrared spectra (4000–400 cm<sup>−1</sup>) of mixtures of BF<sub>3</sub> with *cis*-2-butene, *trans*-2-butene and 2-methylpropene, dissolved in liquefied argon (88–127 K), have been investigated. In all spectra, evidence was found for the formation of a 1:1 van der Waals complex, while at higher concentrations of BF<sub>3</sub> weak bands indicating the presence of a 1:2 complex were also observed. Using spectra recorded at different temperatures, the complexation enthalpies  $\Delta H^\circ$  for *cis*-2-butene·BF<sub>3</sub>, *trans*-2-butene·BF<sub>3</sub> and 2-methylpropene·BF<sub>3</sub> were determined to be −12.5(2), −12.4(2) and 12.7(2) kJ mol<sup>−1</sup>, respectively. For all 1:1 complexes studied, the equilibrium geometry and the vibrational frequencies were obtained from density functional calculations at the B3LYP/6-311++G(d,p) level. Using statistical thermodynamics to account for the zero-point vibrational and thermal contributions, the complexation enthalpies of the 1:1 complexes were transformed into complexation energies  $\Delta E$ . The resulting values, −14.5(4), −14.9(5) and −14.8(5) kJ mol<sup>−1</sup>, respectively, are compared with the values predicted at the B3LYP/6-311++G(d,p) and the BSSE corrected MP2/6-311++G(3df,2pd)//B3LYP/6-311++G(d,p) levels. © 2000 Elsevier Science B.V. All rights reserved.

**Keywords:** van der Waals molecules; Infrared spectroscopy; Ab initio calculations; Cryosolutions

## 1. Introduction

A wide range of Lewis acids has been employed as effective catalysts for organic and inorganic reactions. One example is the Friedel Crafts alkylation reaction, where, amongst others, boron trifluoride is used [1]. It is usually postulated that the catalytic reaction is due to the formation of an initial molecular complex, in

which the Lewis acid distorts and activates the Lewis base, increasing its susceptibility to reaction. Therefore, the study of these complexes is of interest if the catalytic action of the Lewis acid is to be understood in detail. These complexes are relatively weak, which makes their experimental study difficult. Under equilibrium conditions, their concentration increases with decreasing temperature, and it has been shown that in cryosolutions, i.e. in liquefied argon and nitrogen, their concentrations are sufficiently high to be detectable by infrared spectroscopy [2,3]. It is in this field that the present study is situated.

Recently, the complexes of the Lewis acid boron trifluoride with the unsaturated hydrocarbons ethene

<sup>☆</sup> Dedicated to Professor James R. Durig on the occasion of his 65th birthday.

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and propene have been studied in cryosolutions [2], but to the best of our knowledge no data on complexes with higher homologs can be found in the literature. It is the aim of this paper to fill this gap by studying cryosolutions of mixtures of boron trifluoride with the three isomeric butenes, *cis*- and *trans*-2-butene and 2-methylpropene. The complexes of hydrogen chloride with these bases have been studied, and their complexation enthalpies in liquid argon were measured to be  $-11.9(5)$ ,  $-11.6(4)$  and  $-11.2(3)$  kJ mol $^{-1}$ , respectively [4]. As expected, these stabilities are quite similar, and are higher than those for ethene-HCl,  $-8.7$  kJ mol $^{-1}$  [5], and propene-HCl,  $-9.3(2)$  kJ mol $^{-1}$  [6]. The increase in stability from ethene to butene is in line with the electron-donor nature of the methyl substituent, which increases the nucleophilicity of the  $\pi$  bond. It is, however, not self-evident that the same systematic trend should occur for the BF $_3$  complexes, as in the latter the steric hindrance between BF $_3$  and the substituents on the  $\pi$  bond may offset the increase in van der Waals bond strength. Combined with the stabilities of the ethene and propene complexes [5,6], the present study will provide the data required to establish the trend.

In the following paragraphs we will discuss the infrared spectra of mixtures, dissolved in liquid argon, of the proposed butenes with boron trifluoride, from which it will become clear that in all cases the formation of a complex is observed. From spectra recorded at several temperatures the complexation enthalpies will be derived, and the experimental data will be interpreted in the light of B3LYP/6-311++G(d,p) and MP2/6-311++G(3df,2pd) ab initio calculations of structures, energies and vibrational frequencies of monomers and complexes.

## 2. Experimental

The samples of *cis*-2-butene, *trans*-2-butene, 2-methylpropene and boron trifluoride were purchased from Aldrich, and Union Carbide, respectively. In the spectra of the alkenes, no impurities could be detected, while small amounts of SiF $_4$  were present as an impurity in the BF $_3$  used. The solvent gas, argon, was provided by L' Air Liquide and had a stated

purity of 99.9999%. All gases were used without further purification.

The IR spectra were recorded on a Bruker IFS 66v Fourier transform spectrometer, using a globar source, a Ge/KBr beamsplitter and a broadband MCT detector. For each spectrum, 200 interferograms were averaged, Happ Genzel apodized, and Fourier transformed with a zero filling factor of four to produce a spectrum with a resolution of 0.5 cm $^{-1}$ .

The cryosolution setup consists of a pressure manifold needed for filling and evacuating the cell and for monitoring the amount of gas used in a particular experiment, and the actual cell, with an optical path length of 70 mm. The latter is equipped with wedged Si windows and can withstand an internal pressure of at least 170 bar at 77 K without leaking.

To be able to distinguish the spectra of dissolved and undissolved species, solid state spectra of the alkenes under study were obtained by condensing a small amount of the compound onto a CsI window, cooled to 10 K using a Leybold Heraeus ROK 10-300 closed cycle cooling system, followed by annealing until no further changes were observed in the infrared spectrum.

The density functional theory calculations were carried out using GAUSSIAN94 [7]. For all calculations, Becke's three-parameter exchange functional [8] was used in combination with the Lee–Yang–Parr correlation functional [9], while the 6-311++G(d,p) basis set was used throughout as a compromise between accuracy and applicability to larger systems. To reduce the errors arising from the numerical integration, for all calculations the finegrid option, corresponding to roughly 7000 grid points per atom, was used.

For the complex species more accurate values for the complexation energy, including corrections for basis set superposition error (BSSE), were obtained from ab initio calculations at the MP2/6-311++G(3df,2pd)//B3LYP/6-311++G(d,p) level.

## 3. Results

### 3.1. Vibrational spectra

The spectra of monomeric *cis*-2-butene (CB), *trans*-2-butene (TB), 2-methylpropene (MP) and

Table 1

Vibrational frequencies of BF<sub>3</sub> modes for *trans*-2-butene·BF<sub>3</sub>, *cis*-2-butene·BF<sub>3</sub> and 2-methylpropene·BF<sub>3</sub> dissolved in liquid argon at 100 K

			<i>cis</i> -2-Butene·BF <sub>3</sub>		<i>trans</i> -2-Butene·BF <sub>3</sub>		2-Methylpropene·BF <sub>3</sub>	
	<sup>10</sup> BF <sub>3</sub>	<sup>11</sup> BF <sub>3</sub>	<sup>10</sup> B	<sup>11</sup> B	<sup>10</sup> B	<sup>11</sup> B	<sup>10</sup> B	<sup>11</sup> B
$\nu_1^{\text{BF}_3}$	a	a	874.1	874.1	875.2	875.2	873.6	873.6
$\nu_2^{\text{BF}_3}$	708.4	679.5	654.1	630.1	664.8	638.2	653.6	630.6
$\nu_3^{\text{BF}_3}$	1495.8	1445.0	1482.8	1430.9	1486.0	1431.6	142.1	1430.4
$\nu_4^{\text{BF}_3}$	470.7	470.7	b	b	1483.6	b	b	b
$\nu_1^{\text{BF}_3} + \nu_4^{\text{BF}_3}$	1358.2	1358.2	1346.3	1346.3	1348.6	1348.6	1345.6	1345.6
$\nu_1^{\text{BF}_3} + \nu_3^{\text{BF}_3}$	2374.9	2324.9	2351.2	2300.9	2355.2	2303.8	2350.0	2302.0
							2348.2	2298.7

<sup>a</sup> Not infrared active, Raman gas phase frequency at 888 cm<sup>-1</sup>.<sup>b</sup> Not observed.

boron trifluoride have been described elsewhere [4,10–14] and will not be discussed in detail here.

The most obvious indications for the formation of a complex are the BF<sub>3</sub> modes, as they allow an immediate comparison between the different butenes studied. The frequencies of the bands observed in this study have been collected in Table 1.

In Fig. 1, the  $\nu_2^{\text{BF}_3}$  region for a solution in liquid Ar containing approximately  $8.0 \times 10^{-3}$  M MP and  $0.4 \times 10^{-3}$  M BF<sub>3</sub> and that of a solution containing only BF<sub>3</sub>

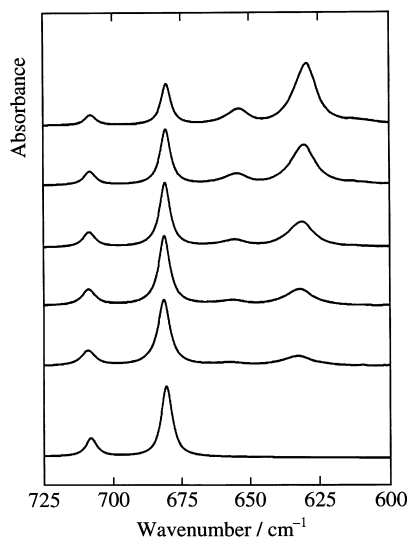


Fig. 1. The  $\nu_2^{\text{BF}_3}$  region for a solution in liquid argon containing 2-methylpropene and BF<sub>3</sub>. The bottom spectrum was recorded from a solution containing only BF<sub>3</sub>. For the other spectra, the temperature of the solution increases, from top to bottom, from 86 to 108 K.

are compared. On the low frequency side of the  $\nu_2^{\text{BF}_3}$  isotopic doublet, with bands situated at 708.4 and 679.5 cm<sup>-1</sup>, for the mixed solutions new bands are observed, at 653.6 and 630.6 cm<sup>-1</sup>, respectively. The new bands prove the formation of a complex and they are assigned to the  $\nu_2^{\text{BF}_3}$  modes of MP·<sup>10</sup>BF<sub>3</sub> and MP·<sup>11</sup>BF<sub>3</sub>, respectively.

A similar comparison for the  $\nu_3^{\text{BF}_3}$  region is made in Fig. 2C. Apart from the monomer absorptions, intense bands are observed at 1482.2 and 1430.4 cm<sup>-1</sup> in the spectrum of the mixed solution. These bands show the same temperature and concentration dependence as the 653.6 and 630.6 cm<sup>-1</sup> bands described in the previous paragraph, and, consequently, are assigned to the BF<sub>3</sub> antisymmetric stretches,  $\nu_3^{\text{BF}_3}$ , in MP·<sup>10</sup>BF<sub>3</sub> and MP·<sup>11</sup>BF<sub>3</sub>, respectively.

Splittings indicating the presence of a complex band were also observed for some of the combination bands and overtones involving  $\nu_2^{\text{BF}_3}$  and  $\nu_3^{\text{BF}_3}$ . For example, for the band at 1358.2 cm<sup>-1</sup>, barely visible in Fig. 2C, which is assigned to  $\nu_1^{\text{BF}_3} + \nu_4^{\text{BF}_3}$  in monomer BF<sub>3</sub>, a new band due to the complex is observed at 1345.6 cm<sup>-1</sup>. Moreover, as can be seen in Fig. 3C, for the combination  $\nu_1^{\text{BF}_3} + \nu_3^{\text{BF}_3}$ , situated in the monomer at 2374.9 cm<sup>-1</sup> (<sup>10</sup>BF<sub>3</sub>) and 2324.9 cm<sup>-1</sup> (<sup>11</sup>BF<sub>3</sub>), new bands due to the corresponding modes in the complex can be observed at a frequency approximately 25 cm<sup>-1</sup> lower than that observed for the monomer species. It should be noted that these bands in fact appear as doublets with maxima located at 2350.0 and 2348.1 cm<sup>-1</sup>, and at 2302.0 and 2298.7 cm<sup>-1</sup>. Although such

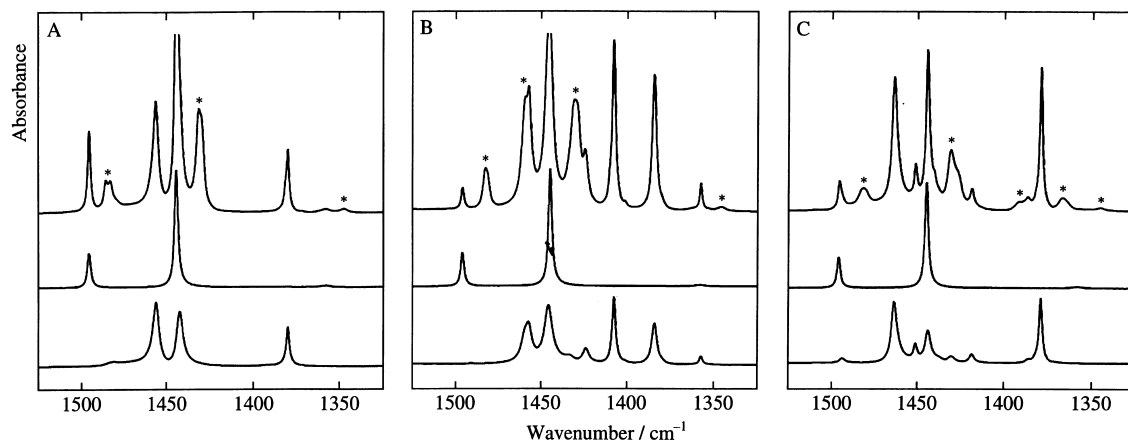


Fig. 2. The  $\nu_3^{\text{BF}_3}$  region for a solution in liquid argon containing *trans*-2-butene and  $\text{BF}_3$  (A), for a solution containing *cis*-2-butene and  $\text{BF}_3$  (B) and for a solution containing 2-methylpropene and  $\text{BF}_3$  (C). The two lower spectra were recorded from a solution containing only  $\text{BF}_3$ , and only *trans*-2-butene, *cis*-2-butene or 2-methylpropene, respectively.

splittings were not observed for the  $\nu_3^{\text{BF}_3}$  fundamentals, the observation of the two bands for each mode shows that in the complex the degeneracy of the  $\text{BF}_3$  antisymmetric stretches is lifted. This is analogous to the splittings observed for, for example, the complex between allene and  $\text{BF}_3$  [15] and that between vinyl fluoride and  $\text{BF}_3$  [16].

Evidently, the formation of a complex must also give rise to new bands due to modes in the base molecules. Some of the more obvious cases are discussed in the next paragraphs.

In Fig. 4, the 920–860  $\text{cm}^{-1}$  and the 1680–1620  $\text{cm}^{-1}$  regions of the spectrum, recorded at different temperatures, of a solution containing both MP and  $\text{BF}_3$  and those obtained for a solution containing only MP are compared. On the high frequency side of the 888.4  $\text{cm}^{-1}$  band, assigned to the  $\text{CH}_2$  wagging mode in MP,  $\nu_{23}^{\text{MP}}$ , a new band due to the corresponding mode in the 1:1 complex appears at 903.1  $\text{cm}^{-1}$  in the spectra of the mixed solution. Moreover, on the low frequency side of the 888.4  $\text{cm}^{-1}$  band, a new band due to the  $\text{BF}_3$

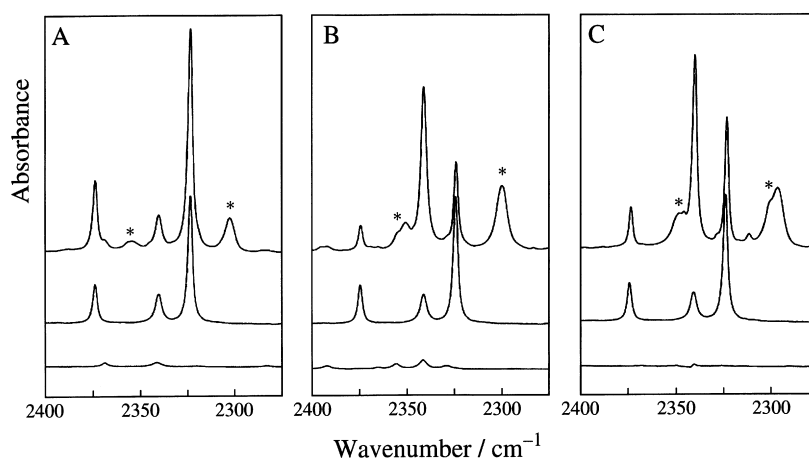


Fig. 3. The  $\nu_1^{\text{BF}_3} + \nu_3^{\text{BF}_3}$  region for a solution in liquid argon containing *trans*-2-butene and  $\text{BF}_3$  (A), for a solution containing *cis*-2-butene and  $\text{BF}_3$  (B) and for a solution containing 2-methylpropene and  $\text{BF}_3$  (C). The two lower spectra were recorded from a solution containing only  $\text{BF}_3$ , and only *trans*-2-butene, *cis*-2-butene or 2-methylpropene, respectively.

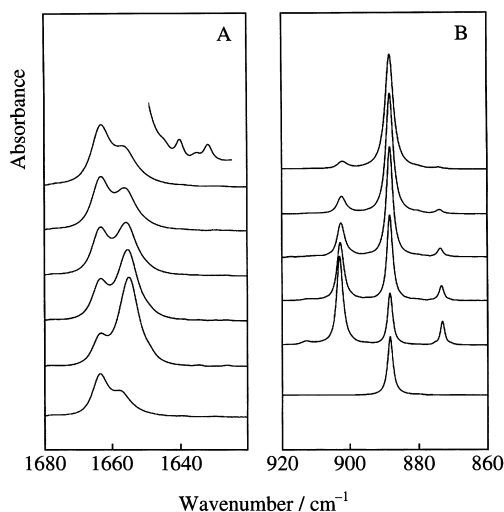


Fig. 4. Details of the mid-infrared spectra of a 2-methylpropene/ $\text{BF}_3$  mixture dissolved in liquid argon. The bottom spectrum in each panel was recorded from a solution containing only 2-methylpropene. For the other spectra, the temperature of the solution increases from bottom to top, from 86 to 108 K.

symmetric stretch in the complex can be observed, at  $873.6\text{ cm}^{-1}$ . This mode is infrared inactive in the monomer, but has induced intensity in the complex. It can also be seen that the relative intensity of the complex bands increases as the temperature is

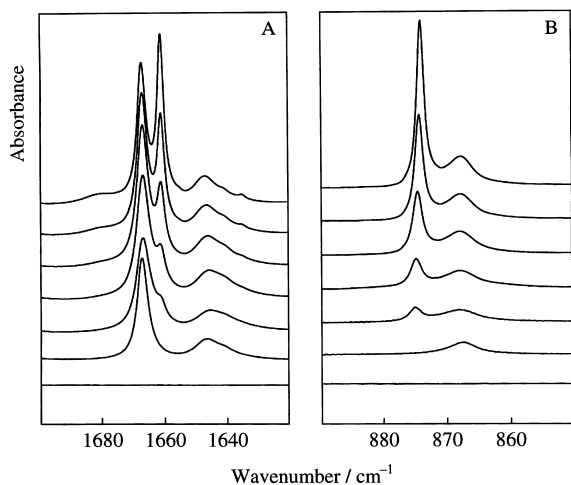


Fig. 5. Details of the mid-infrared spectra of a *cis*-2-butene/ $\text{BF}_3$  mixture dissolved in liquid argon. The bottom spectra were recorded from a solution containing only  $\text{BF}_3$  and *cis*-2-butene. From top to bottom, for the other spectra, the temperature of the solution increases from 85 to 113 K.

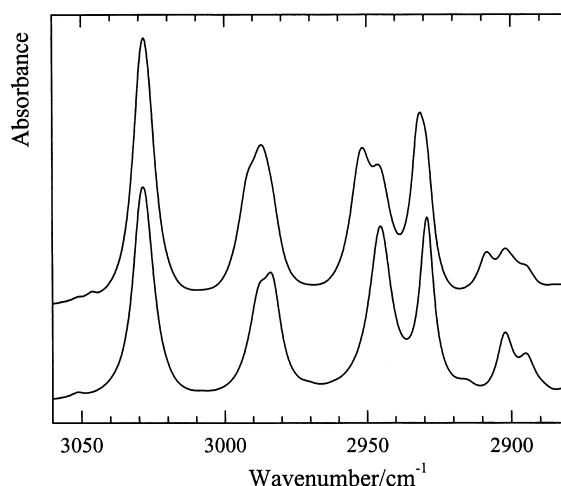


Fig. 6. The C–H stretching region for a solution in liquid argon, at 94 K, containing *cis*-2-butene and  $\text{BF}_3$  (top) and for a solution containing only *cis*-2-butene (bottom).

lowered. This is as expected for a solution in which the monomers are in chemical equilibrium with the complex.

At the lowest temperatures, in the spectra shown in Fig. 4B, very weak features emerge at  $912.5$  and  $875.7\text{ cm}^{-1}$ . Because these bands only appear for solutions containing larger amounts of  $\text{BF}_3$ , we assign them to a higher complex, in which two  $\text{BF}_3$  molecules are bonded with a single MP molecule:  $\text{MP} \cdot (\text{BF}_3)_2$ .

The spectra shown in Fig. 5A illustrates that also for the C=C stretching fundamental in MP,  $\nu_4^{\text{MP}}$ , originally situated at  $1663.8\text{ cm}^{-1}$ , and the same mode in  $(\text{CH}_3)_2^{13}\text{C}=\text{CH}_2$  and  $(\text{CH}_3)_2\text{C}=\text{CH}_2^{13}$ , located at  $1639.3$  and  $1629.7\text{ cm}^{-1}$ , respectively, new bands due to the 1:1 complexes can be observed, at  $1655.4$ ,  $1634.8$  and  $1623.6\text{ cm}^{-1}$ . From the fact that the complex bands appear on the low frequency side of the monomer bands, it can be anticipated that the complexation with  $\text{BF}_3$  slightly weakens the C=C bond in MP.

By analogy with the results obtained for MP, for the solutions containing mixtures of CB and  $\text{BF}_3$  and of TB and  $\text{BF}_3$ , new bands signalling the presence of a 1:1 complex were observed, in the  $\nu_1^{\text{BF}_3}$ , the  $\nu_2^{\text{BF}_3}$ , the  $\nu_3^{\text{BF}_3}$  and the  $\nu_1^{\text{BF}_3} + \nu_3^{\text{BF}_3}$  regions. In Figs. 2A and B, 3A and B and 6, the  $\nu_1^{\text{BF}_3}$ , the  $\nu_3^{\text{BF}_3}$  and the  $\nu_1^{\text{BF}_3} + \nu_3^{\text{BF}_3}$  regions of a typical solution containing both TB and

BF<sub>3</sub>, and that of a solution containing both CB and BF<sub>3</sub> are shown.

The spectra in Fig. 5B illustrate that for mixtures of CB and BF<sub>3</sub>, a complex band appears, at approximately 874.1 cm<sup>-1</sup>. This band must be assigned to either the BF<sub>3</sub> symmetric stretch in the complex,  $\nu_1^{\text{BF}_3}$ , or to the same mode as that causing the 867.3 cm<sup>-1</sup> band in monomer CB,  $\nu_9^{\text{BF}_3}$ . Density functional calculations at the B3LYP/6-311++G(d,p) level predict (vide infra) that upon complexation with BF<sub>3</sub> the frequency of  $\nu_9^{\text{CB}}$  hardly changes, the predicted values for monomer and complex being 866.8 and 867.3 cm<sup>-1</sup>, respectively. The predicted infrared intensities for  $\nu_9^{\text{CB}}$  in monomer CB and in CB·BF<sub>3</sub>, 0.48 and 0.49 km mol<sup>-1</sup>, are significantly smaller than the value of 3.30 km mol<sup>-1</sup> calculated for  $\nu_1^{\text{BF}_3}$  in the complex. In view of these results, and taking into account the fact that a similar band was also observed for the solutions containing MP, we assign the 874.1 cm<sup>-1</sup> band to the BF<sub>3</sub> symmetric stretch in CB·BF<sub>3</sub>.

In Fig. 5A, the C=C stretching region for a solution containing CB and BF<sub>3</sub>, recorded at different temperatures, and that of a solution containing only monomer species are compared. On the low frequency side of the 1667.1 cm<sup>-1</sup> band, assigned to the C=C stretching fundamental in CB,  $\nu_4^{\text{CB}}$ , in the spectra of the mixed solution, a new band due to the corresponding mode in the complex is observed, at 1661.5 cm<sup>-1</sup>. Apart from this, new bands due to CB·BF<sub>3</sub> are also observed near 1680 and 1634 cm<sup>-1</sup>. We assign the former band to the same mode as the one causing the 1646.3 cm<sup>-1</sup>  $\nu_{19}^{\text{CB}}$  band, while the weak feature near 1634 cm<sup>-1</sup> is correlated with the very weak monomer absorption at 1640.7 cm<sup>-1</sup>.

Fig. 6 contains the CH stretching region of CB and of a CB/BF<sub>3</sub> mixture, both recorded at 94 K. Before discussing the complex bands appearing in this region, it appears necessary that we comment on the assignments of monomer CB. The CH stretching region of this compound has been described in detail in two studies [10,11] but comparison shows that the authors disagree on all but one of the assignments of the eight fundamentals that are present in this region. On the basis of our own gas phase measurements, we are inclined to adhere largely to the assignments proposed by McKean et al. [10], for the following reasons (the use of the Herzberg numbering in this discussion would be confusing, and, therefore, we

will employ the localized description used by the previous authors [10,11], indicating the Herzberg numbering, where appropriate, in brackets).

The olefinic CH stretches were assigned in Ref. [11] at 3038 cm<sup>-1</sup> ( $\nu_{\text{CH}}$ , A<sub>1</sub>) and at 3023 cm<sup>-1</sup> ( $\nu_{\text{CH}}$ , B<sub>2</sub>). The minimum between these bands, at 3031.5 cm<sup>-1</sup>, was identified in Ref. [10] as the band center of the type B band due to  $\nu_{\text{CH}}$ , A<sub>1</sub> ( $\nu_1$ ). We have simulated the type B contour using the rigid asymmetric top approximation [17], starting from the ab initio rotational constants, and have found that its contour is in excellent agreement with the experimental contour in this region, the PQ and QR branches of which were assigned in Ref. [11] to the two fundamentals. Hence, our results support the assignment of Ref. [10]. The  $\nu_{\text{as}}\text{CH}_3$ , B<sub>2</sub> was assigned in Ref. [11] at 2948 cm<sup>-1</sup>, while the band contour clearly is type C, implying that this band is actually  $\nu_{\text{as}}\text{CH}_3$ , B<sub>1</sub> ( $\nu_{17}$ ). The band at 2935 cm<sup>-1</sup>, assigned in Ref. [11] to  $\nu_{\text{as}}\text{CH}_3$ , A<sub>1</sub> has a well-defined type A contour, and therefore has to be due to a fundamental of symmetry B<sub>2</sub> ( $\nu_{24}$ ). The symmetric CH<sub>3</sub> stretches are assigned in Ref. [11] to bands at 2876 and 2870 cm<sup>-1</sup>, which have been shown by McKean et al. [10] to be overtones, the intensities of which are enhanced by Fermi resonance with the symmetric stretches  $\nu_{\text{s}}\text{CH}_3$ , A<sub>1</sub> ( $\nu_3$ ) and  $\nu_{\text{s}}\text{CH}_3$ , B<sub>2</sub> ( $\nu_{24}$ ), the latter being accidentally degenerate at 2935 cm<sup>-1</sup>.

We do not fully agree, however, with the assignments of McKean et al. [10] in the region between 3000 and 2950 cm<sup>-1</sup>. Here, in Ref. [10] a strong band at 2973 cm<sup>-1</sup>, which the authors tabulate as having a type B contour, is assigned to  $\nu_{\text{CH}}$ , B<sub>2</sub>. The listed band type and the assigned symmetry obviously are incompatible. Moreover, the maximum at 2973 cm<sup>-1</sup> corresponds to the P branch of a type A band, the Q branch of which in our spectra can clearly be distinguished at 2986 cm<sup>-1</sup> (in fact, this Q branch can be seen in the spectrum shown in Fig. 2 of Ref. [11], but the authors fail to identify it in their Table 1). The observed type A band must be due to  $\nu_{\text{CH}}$ , B<sub>2</sub> ( $\nu_{22}$ ). The transition in this region in the liquid Ar spectrum is a strongly overlapping doublet, consisting of transitions with similar intensities, at 2987 and 2984 cm<sup>-1</sup>. Our ab initio calculations predict infrared intensities of 16 km mol<sup>-1</sup> for  $\nu_{\text{CH}}$ , B<sub>2</sub> and of 13 km mol<sup>-1</sup> for  $\nu_{\text{as}}\text{CH}_3$ , A<sub>1</sub>. Therefore, we assign the slightly weaker second component, at 2987 cm<sup>-1</sup>, as the A<sub>1</sub> ( $\nu_2$ )

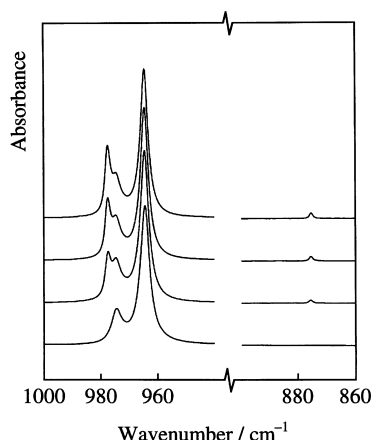


Fig. 7. Details of the mid-infrared spectra of a *trans*-2-butene/BF<sub>3</sub> mixture dissolved in liquid argon. The bottom spectrum was recorded from a solution containing only *trans*-2-butene. From top to bottom, for the other spectra, the temperature of the solution increases from 100 to 121 K.

fundamental. This transition must give rise to a type B band in the vapor phase. Its near degeneracy with  $\nu\text{CH}$ , B<sub>2</sub> ( $\nu_{22}$ ), and the similarity of the PR separation of the type A transition with the PQ–QR separation of the type B cause  $\nu_{\text{as}} \text{CH}_3$ , A<sub>1</sub> ( $\nu_2$ ) to remain unobserved in the vapor phase spectrum.

Finally, in this region  $\nu_{\text{as}} \text{CH}_3$ , B<sub>2</sub> remains to be identified. The *ab initio* calculations predict its intensity to be approximately a third of that of  $\nu\text{CH}$ , B<sub>2</sub>. If the calculated relative intensities are correct, a type A band should be detectable. However, no feature assignable to a type A band can be distinguished in this region of the vapor phase spectrum. In liquid argon, a very weak band is detected at 2969 cm<sup>-1</sup>, whose relative intensity compared with the  $\nu\text{CH}$ , B<sub>2</sub>/ $\nu_{\text{as}} \text{CH}_3$ , A<sub>1</sub> doublet is much smaller than the *ab initio* value. The tentative assignment of this band to  $\nu_{\text{as}} \text{CH}_3$ , B<sub>2</sub> ( $\nu_{23}$ ) is, therefore, not incompatible with the vapor phase observations.

The spectrum of the mixture in Fig. 6 was recorded from a solution containing a large excess of BF<sub>3</sub>. At the temperature and concentrations used, the larger fraction of the CB molecules is transformed into a 1:1 complex, and new bands due to the latter, at 2951.6 and 2908.4 cm<sup>-1</sup>, are obvious on a first visual comparison. Closer inspection shows that several, more subtle ones can be detected.

For the highest fundamental in this region,  $\nu_1$ , no

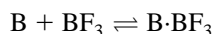
shift of the band is observed for the mixture, from which is concluded that the complex and monomer bands occur accidentally degenerate, in agreement with the complexation shift of + 1.2 cm<sup>-1</sup> predicted by the *ab initio* calculations. For the  $\nu_2/\nu_{22}$  doublet, the calculations predict shifts of + 4.9 and + 3.1 cm<sup>-1</sup>, respectively. For the mixture, the components are observed at 2992.0 and 2987.0, shifted by + 4.2 and + 3.1 cm<sup>-1</sup>, from the monomer frequencies, neatly in line with the predictions. The complex band for  $\nu_{17}$  at 2951.6 cm<sup>-1</sup> is shifted by + 6.3 cm<sup>-1</sup> from its monomer position, while the predicted shift is + 10.8 cm<sup>-1</sup>. For the accidentally degenerate couple  $\nu_3/\nu_{24}$ , the predicted shifts are + 6.1 and + 6.5 cm<sup>-1</sup>, respectively. In agreement with this, a single complex band is observed in this region for the mixture, at 2931.4, 2.4 cm<sup>-1</sup> above the monomer frequency.

The formation of complexes between TB and BF<sub>3</sub> is illustrated in Fig. 7, where the 1000–860 cm<sup>-1</sup> region of a solution of the mixture, recorded at temperatures between 111 and 118 K, and that of a solution containing only TB are compared. On the high frequency side of the 965.0 and the 975.1 cm<sup>-1</sup> monomer bands, assigned to  $\nu_{19}^{\text{TB}}$  (A<sub>u</sub>) and  $\nu_{29}^{\text{TB}}$  (B<sub>u</sub>), respectively, a new band due to the  $\nu_{19}^{\text{TB}}$  mode in the complex is observed at 977.8 cm<sup>-1</sup>. The spectra in Fig. 7 further show that for the complex between TB and BF<sub>3</sub>, a weak, interaction-induced  $\nu_1^{\text{BF}_3}$  is observed, at 875.2 cm<sup>-1</sup>.

For TB, the C=C stretching mode,  $\nu_4^{\text{TB}}$ , is infrared inactive. The weak band at 1671 cm<sup>-1</sup> observed for the mixture is assigned to this mode in the complex, its activity also being interaction induced.

### 3.2. Complexation enthalpy

Using the equilibrium constant for the complexation reaction between a Lewis base B and BF<sub>3</sub>:



and making the usual assumptions [18], it is easily shown that

$$\ln\{I_{\text{B} \cdot \text{BF}_3}/I_{\text{B}} \times I_{\text{BF}_3}\}$$

is linearly related to  $1/T$ , the slope of this relation being  $-\Delta H^\circ/R$ , in which  $\Delta H^\circ$  is the standard complexation enthalpy. Hence, by plotting the above



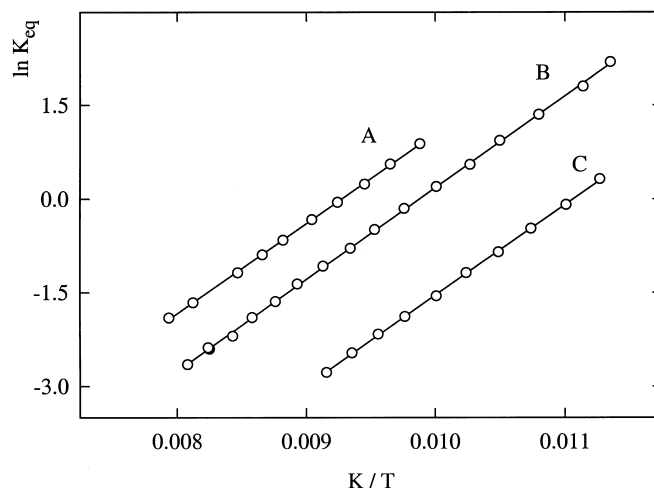


Fig. 8. Van 't Hoff plots for *trans*-2-butene-BF<sub>3</sub> (A), *cis*-2-butene-BF<sub>3</sub> (B) and 2-methylpropene-BF<sub>3</sub> (C) dissolved in liquid argon.

logarithm versus the inverse temperature, the stability of both complexes, expressed as an enthalpy difference  $\Delta H^\circ$ , can be obtained.

In this study infrared spectra of solutions containing both the appropriate alkene and BF<sub>3</sub> were recorded at several temperatures, between 100 and 127 K (TB), between 85 and 125 K (CB) and between 86 and 110 K (MP). For all alkenes studied, the intensities for the complex,  $I_{B-BF_3}$ , and for monomeric BF<sub>3</sub>,  $I_{BF_3}$ , were taken from a least-squares band fitting, using Gauss/Lorentz sum profiles, of the  $\nu_1^{BF_3} + \nu_3^{BF_3}$  region, while for the monomer intensities  $I_{TB}$ ,  $I_{CB}$  and  $I_{MP}$ , the integrated intensities of 964.7, 1667.4 and 888.5 cm<sup>-1</sup> monomer bands, respectively, were used.

The resulting van 't Hoff plots obtained for the 1:1

complexes are shown in Fig. 8. From the slopes of the linear regressions, corrected for the density variations of the solution [18], complexation enthalpies  $\Delta H^\circ$  of -12.5(2) (CB-BF<sub>3</sub>), -12.4(2) (TB-BF<sub>3</sub>), and -12.7(2) kJ mol<sup>-1</sup> (MP-BF<sub>3</sub>) were calculated.

### 3.3. *Ab initio* calculations

To gain insight into the structures of the different complexes and their relative stabilities, for the 1:1 complexes the equilibrium geometry and the vibrational frequencies were calculated, using density functional calculations at the B3LYP/6-311++G(d,p) level. The resulting equilibrium structures and their interaction energies, defined as the

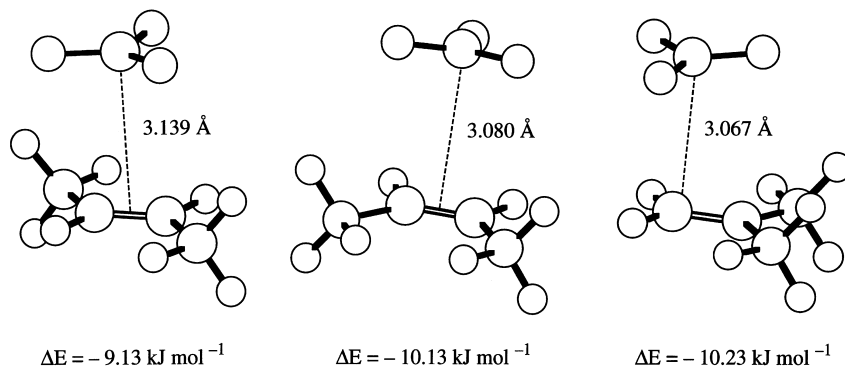


Fig. 9. The B3LYP/6-311++G(d,p) equilibrium structures, van der Waals bond lengths and complexation energies for *trans*-2-butene-BF<sub>3</sub>, *cis*-2-butene-BF<sub>3</sub> and 2-methylpropene-BF<sub>3</sub>.

energy of the complex from which the monomer energies have been subtracted, are shown in Fig. 9. In view of the large number of internal coordinates needed to define the different equilibrium geometries, in this study no detailed analysis of the calculated equilibrium geometries will be reported. These data, together with the calculated frequencies and intensities, are available from the authors upon request.

For all alkenes studied, the calculations converge to a structure similar to the one obtained for ethene·BF<sub>3</sub> [2], i.e. one in which the electron deficient boron atom interacts with the  $\pi$  bond. The intermolecular distance  $R_{\text{vdW}}$  is defined as the distance between the boron atom and its perpendicular projection on the line connecting the carbon atoms of the  $\pi$  bond.

The butenes studied here represent the different ways in which two methyl substituents can be distributed between the two olefinic carbon atoms. A methyl substituent exerts a larger steric hindrance than a hydrogen atom, and this can be used to rationalize the differences in the calculated structures. For MP, the combined steric hindrance of the two methyl groups causes the van der Waals bond to shift by 0.84 Å away from the center of the  $\pi$  bond, towards the =CH<sub>2</sub> grouping. In the case of *cis*-2-butene the steric hindrance is minimized by rotating away the BF<sub>3</sub> moiety: the angle between the van der Waals bond and a line perpendicular to the plane of the four carbon atoms is 13°. The similarity of the van der Waals bond length and complexation energy with those of the MP complex suggests that both ways of reducing steric hindrance are very nearly equally efficient. Neither of these ways, however, works for *trans*-2-butene. As a consequence, in this complex the van der Waals bond is significantly longer, and its ab initio complexation energy is somewhat smaller.

#### 4. Discussion

The experimental enthalpies contain solvent influences and zero-point vibrational and thermal contributions and, therefore, cannot be straightforwardly compared with the ab initio complexation energies. Using Monte Carlo calculations based upon free enthalpy perturbation theory [19–22], it can be shown [23] that, although the interactions between

the solute molecules and the surrounding rare gas atoms cannot be neglected, the solvent has a minor influence on the complexation enthalpies. Hence, to a first approximation, we will take the vapor phase enthalpies to be equal to the solution values.

To account for the zero-point vibrational and thermal influences, for all 1:1 complexes, the vapor phase  $\Delta H^\circ$  was transformed into a complexation energy  $\Delta E$ , using straightforward statistical thermodynamics. The zero-point vibrational energies were calculated using the B3LYP/6-311++G(d,p) ab initio frequencies. In addition, thermal contributions were calculated at the mid-point of the temperature interval in which  $\Delta H^\circ$  was determined in liquid Ar. Translational and rotational thermal contributions were calculated in the classical limit, and vibrational thermal contributions were calculated in the harmonic approximation [24] using the same frequencies as for the zero-point corrections. These quantities were used to transform the vapor phase enthalpies into “experimental” complexation energies. The resulting values are –14.8(5) kJ mol<sup>–1</sup> for TB·BF<sub>3</sub>, –14.6(4) kJ mol<sup>–1</sup> for CB·BF<sub>3</sub> and –14.8(4) kJ mol<sup>–1</sup> for MP·BF<sub>3</sub>. The uncertainties quoted have, somewhat arbitrarily, been chosen to be twice those of  $\Delta H^\circ$  in LAr, to account for the approximate nature of the transformation of an enthalpy into an energy.

Accurate ab initio values for the complexation energies were obtained by including dispersion interactions via second order Møller–Plesset perturbation theory. For each species, starting from the DFT geometries, single point calculations were made at the MP2 = full/6-311++G(3df,2pd) level. The complexation energies obtained from these calculations, after correction for BSSE, are –16.0 kJ mol<sup>–1</sup> for TB·BF<sub>3</sub>, –16.5 kJ mol<sup>–1</sup> for CB·BF<sub>3</sub> and –16.3 kJ mol<sup>–1</sup> for MP·BF<sub>3</sub>. It is clear that, in agreement with previous experience [16,25], these values compare favorably with the experimental ones.

The limits of uncertainty of the complexation enthalpies of the butenes studied here overlap, as do those of the experimental complexation energies. From this it may be concluded that the three  $\pi$  systems exhibit nearly identical nucleophilicities. Although the spread in the BSSE corrected values quoted above is slightly higher, it is a mere three percent of the lowest complexation energy, which

means that the ab initio results support the experimental observations.

The complexation enthalpies of the  $\text{BF}_3$  complexes with ethene and propene are  $-10.0(2)$  and  $-11.8(2) \text{ kJ mol}^{-1}$ , respectively. With an average  $\Delta H^\circ$  of  $-12.5(2) \text{ kJ mol}^{-1}$ , for the present  $\pi$  systems, it follows that the stability of the complexes increases systematically with the number of methyl substituents on the olefinic carbon atoms. For the  $\text{HCl}$  complexes, as observed above, a similar trend is found [4–6]. For the latter, the largest increase in stability occurs from propene to the butenes, while for the  $\text{BF}_3$  complexes this increase is significantly smaller than that between ethene and propene. It cannot be excluded that this, as suggested in Section 1, is due to the higher importance of steric hindrance in the  $\text{BF}_3$  complexes compared with the  $\text{HCl}$  complexes.

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