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Study of the radical chemistry promoted by tributylborane

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Abstract The structures of radicals generated in the oxidation process of trialkylborane were detected based on ultra-high performance liquid chromatography-quadrupole-time-of-flight mass spectrometry (UPLC/Q-ToF MS) combined with the spin trapping method. Structural identification of the spin adducts produced by 5,5-dimethyl-1-pyrroline-1-oxide with radicals could be carried out unambiguously by combining the data obtained by UPLC/Q-ToF MS analyses. Then the oxidation mechanism was described. To specify the inter-relationships between the oxidation process of trialkylborane and the concomitant radical chemistry, four kinds of alkanes providing different H-abstraction reactivity to alkoxy radical were chosen as radical capturers. The final oxidation products of trialkylborane were characterized by GC–MS and ^{11}B-NMR. The results indicted that the radical content was not only affected by the oxidation degree of trialkylborane, but also done by the activity of alkane. Especially the hydrogen atom abstraction by *n*-butoxy radical played an important role in the oxidation process of tributylborane, which would promote the oxidizability of tributylborane and deepen the oxidation degree of tributylborane.

Keywords Oxygen · Oxidation · Radical · Trialkylborane · Mechanism

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Introduction

The ability of organoborane to participate in free radical processes has been identified since the earliest investigation of its chemistry [1–3]. Trialkylborane has been used as a radical initiator in the field of adhesives [4–6], polymerization [7–12], grafting [13, 14], and others [15, 16]. The oxidation mechanism of trialkylborane has been studied for several decades. It is assured that the radical chemistry promoted by trialkylborane is triggered by the initial oxidation of trialkylborane to peroxyborane $R_2B(OOR)$, but the generation process of radicals is a controversial issue. Two speculations have been proposed so far: the first is that an alkoxy radical and a borinate radical are produced through the homolytic cleavage of peroxyborane (Eq. 1) [3, 17]. The second is that an alkyl radical and a peroxyborane radical are produced through the heterolytic cleavage of peroxyborane (Eq. 2) [18, 19].

$$R_2B(OOR) \rightarrow R_2BO^{\bullet} + RO^{\bullet} \quad (1)$$

$$R_2B(OOR) \rightarrow R_2BOO^{\bullet} + R^{\bullet} \quad (2)$$

There is no confirmation of the radical chemistry since the oxidation process of trialkylborane is very complex and not controllable, and the structures of generated radicals are hard to determine by the often-used ESR method due to the ESR spectra of different radicals with similar hyperfine splitting constants.

In this study, we utilized the UPLC/Q-ToF MS/MS technique to identify the radicals formed from the oxidation of trialkylborane, and obtained more information for the oxidation mechanism of trialkylborane. On the other hand, the interrelationships between the oxidation degree of trialkylborane and the concomitant radical chemistry were reported. Four kinds of alkanes with different C–H reactivity were used to study in detail the interactions between the oxidation degree of trialkylborane and the concomitant radical chemistry. The comprehensive conclusions from both experiments and theories would be a reliable theoretical basis for the applications of trialkylborane, such as promoting grafting and adhesion.

Materials and methods

1,1-Diphenyl-2-picrylhydrazine (DPPH) and 5,5-dimethyl-1-pyrroline-1-oxide (DMPO) were obtained from Sigma-Aldrich. Both were used without further treatment. Tributylborane (TBB), 1 mol/L in ethyl ether, could be purchased from Aldrich and distilled under vacuum at 50 °C to remove ethyl ether before being used. Alkane compounds: 3-methylpentane, *n*-decane, and squalane were all from Alfa Aesar and 2,4-dimethylpentane was obtained from Tokyo Chemical Industry Co., Ltd. They were used directly.

The oxidation process of tributylborane

Alkane and tributylborane were charged into an argon-filled flask with a magnetic stirrer. The molar ratio of alkane to tributylborane was kept at 10:1. Half an hour

later, oxygen was injected slowly at the rate of 10 mL/h. The reaction was allowed to proceed overnight at 30 °C.

UPLC/Q-ToF MS/MS analysis

The reaction mixture, containing 7.5 μmol DMOP, 1.5 μmol tributylborane and 50 mL acetonitrile, was stirred in a beaker at room temperature for 3 min. The reaction mixture was filtered and injected into the UPLC column for UPLC/Q-ToF MS/MS measurements.

Evaluation of the concentration of free radicals

A 0.5-mL ethanol solution of tributylborane (3.0×10^{-2} mol/L) and 5 mL ethanol solution of DPPH (2.0×10^{-4} mol/L) was added to an argon-filled flask, and then a different amount of oxygen was introduced (0, 2, 4, 5, 10, 15, 30, and 50 mL). The mixture was shaken vigorously and allowed to stand for 20 min in the dark. The decrease in absorbance was measured at 515 nm against a blank (ethanol) with a spectrophotometer.

Characterization

Gas chromatography and mass spectrometry (GC–MS) measurements were performed on a QP2010 GC–MS. Conditions were as follows: column: DB-5 0.25 mm × 0.25 μm × 30 m, column pressure: 10.1 psi, flow-rate: 1.22 mL/min, injector temperature: 280 °C. Temperature of the column: kept 3.5 min at 50 °C and then increased to 250 °C at 20 °C/min, holding for 17 min scan: 33–750 amu.

HPLC/Q-ToF MS/MS was performed on UPLC Acquity/QToF MS Premier (Waters, America). The conditions were: flow rate: 0.2 mL/min, max pressure: 15,000 psi, column temperature: 25 °C, mass range: *m*/*z*: 50–500, ion mode: positive ion mode.

Nuclear magnetic resonance spectroscopy (NMR) was run on Avance-400 (Bruker, Switzerland) at 25 °C. Boric acid was used as external standard, and $CDCl_3$ was used as a solvent.

Results and discussion

DMPO is a widely used nitrone spin trap, which can trap not only carbon-centered radicals but also oxygen-centered radicals [20]. The addition of a reactive free radical across the double bond of DMPO formed a much more stable radical. These spin-trapped radical species are hard to distinguish, since various radical-derived nitroxides show similar ESR spectra. HPLC separation with MS detection has proven reliable in distinguishing the different DMPO/radical adducts. We firstly conducted experiments for the spin trapping of radicals generated from the oxidation of tributylborane in which the identification of the DMPO adducts was

carried out by UPLC/Q-TOF MS and the resulted TIC spectrum was showed in Fig. 1.

The mass profile of the species with a mass-to-charge ratio (*m*/*z*) of 186 could be assigned to the protonated DMPO/·OC_4H_9 adduct (Fig. 2). All the major fragment ions in the MS spectrum were in agreement with the fragmentation pathways of the DMPO/·OC_4H_9 adduct (Scheme 1).

Meanwhile, the mass profile of the specie with a mass-to-charge ratio (*m*/*z*) of 170 was also found and illustrated in Fig. 3, and the major fragment ions in its MS spectra were speculated as Scheme 2, which were assigned to the DMPO/·C_4H_9 adduct.

The UPLC/Q-TOF MS analysis revealed that both *n*-butyl radial and *n*-butoxy radical were produced in the oxidation process of tributylborane, and indicated that the peroxyborane should be homolytic cleavage after the initial oxidation of tributylborane because the electron-withdrawing from the neighboring borane moiety weakened the O–O bond (Eq. 1). The *n*-butyl radical was formed through

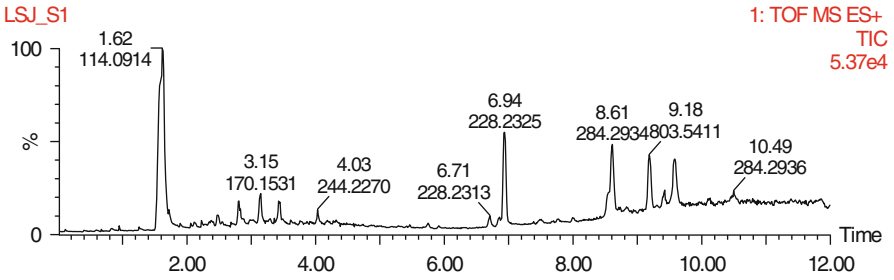


Fig. 1 UPLC/Q-TOF MS chromatogram of the product of DMPO with TBB

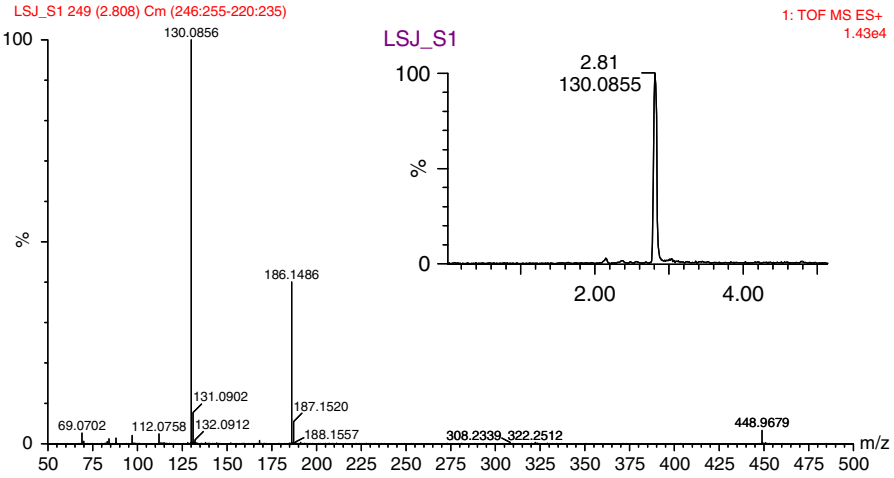
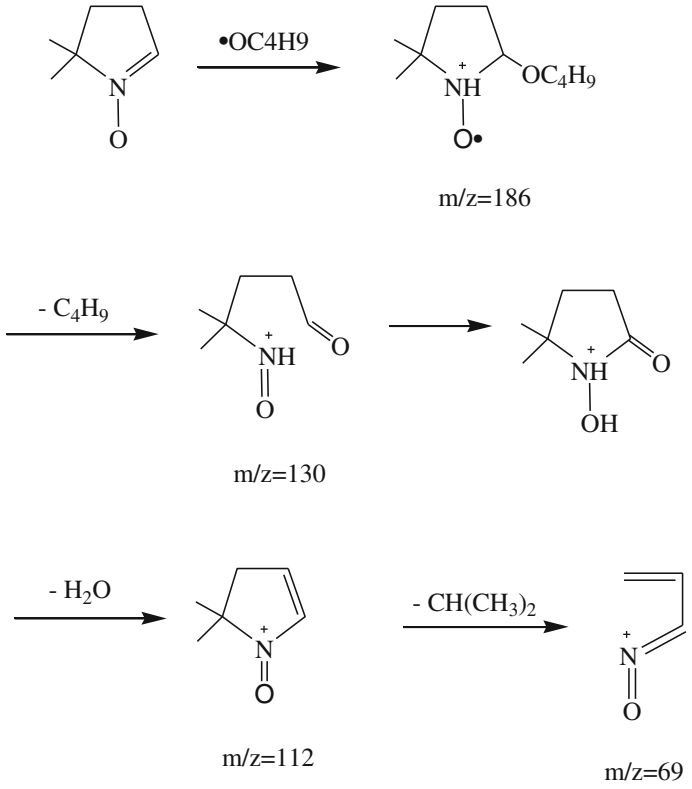


Fig. 2 UPLC/Q-TOF MS analysis of the product of DMPO/·OC_4H_9 adduct



Scheme 1 Proposed fragmentation pathways of the protonated ions DMPO/·OC_4H_9 adduct

the SN1 electronic donating substitution of *n*-butoxy radical (Eq. 3) or the trimerization of borinate radicals (Eq. 4). The latter was the main source of *n*-butyl radical due to the high reactive of tributylborane.

$$BuO^{\bullet} + Bu_3B \rightarrow Bu_2B(OBu) + Bu^{\bullet} \quad (3)$$

$$3Bu_2BO^{\bullet} \rightarrow Bu_3B_3O_3 + 3Bu^{\bullet} \quad (4)$$

For further proving the above mechanism, four kinds of alkanes with different C–H activities (shown in Scheme 3) were used as the capturers of *n*-butoxy radical due to the strong hydrogen atom abstraction ability of *n*-butoxy radical. The oxidation process of trialkylborane was carried out in serious alkanes at room temperature. Then the formations of coupling and hydrogen atom abstraction of generated radicals were separated and distinguished by GC–MS chromatogram. Two of the TIC spectra are shown as Figs. 4 and 5.

N-butanol, *n*-octane, and 2,4,6-tributylboroxin were all detected from the reaction products of tributylborane and alkanes. The results suggested the generation of *n*-butoxy, *n*-butyl, and borinate radicals in the oxidation process of tributylborane. In the alkane compound, *n*-butoxy radical was proposed to abstract hydrogen atom from alkane, thereby yielding a carbon-centered radical on the alkane. *N*-butyl

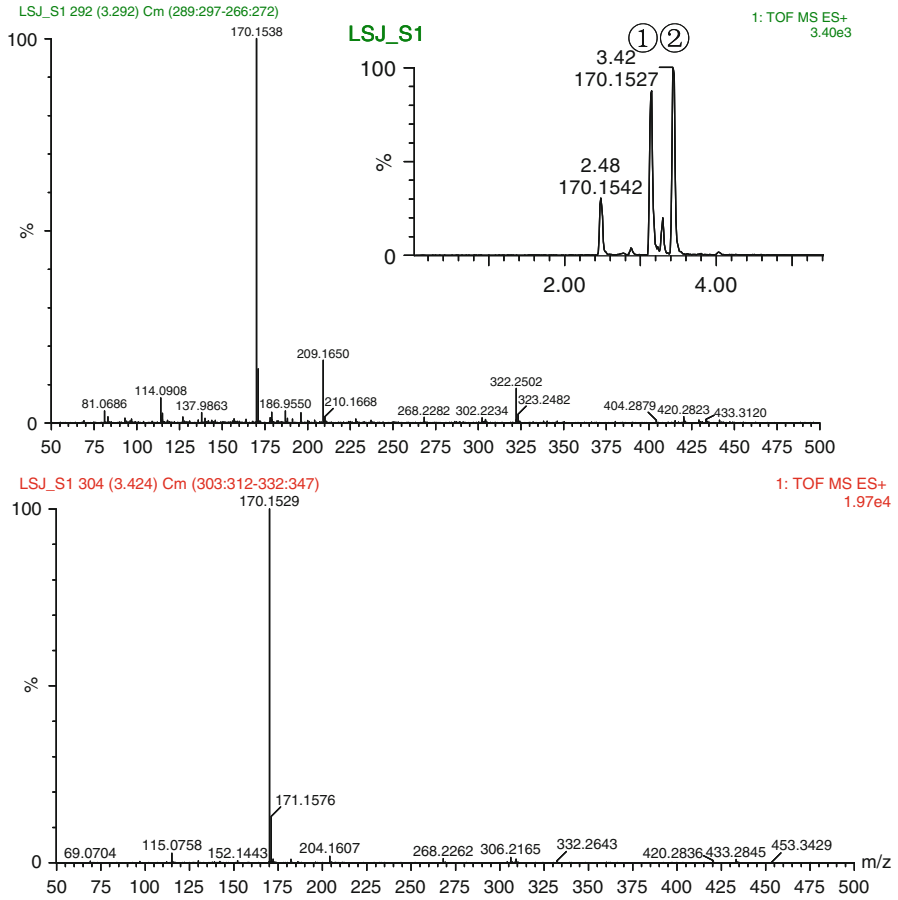
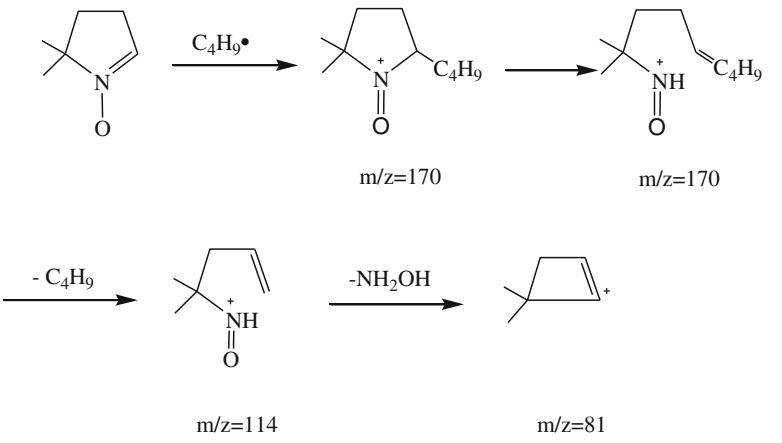


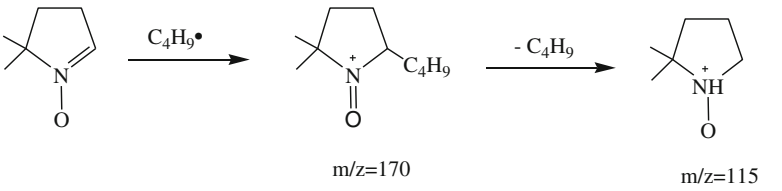
Fig. 3 UPLC/Q-TOF MS analysis of the product of DMPO/·C_4H_9 adduct

radical was not energetic enough to react with alkane, instead, it tended to couple with another radical or to be oxidized. The only one form organoborane found in this system was accounted for the peak ascribed to tributylboroxin, which was the trimerization product of borinate radicals. This cyclic structure was full proof of the homolytic cleavage of the peroxyborane after tributylborane undergoing a single oxidation by oxygen. The changes of *n*-butoxy radical and *n*-butyl radical with oxidation degree of tributylborane could be speculated from the various trends of *n*-butanol and *n*-octane, respectively (Table 1). At the low oxidation degree of tributylborane, more un-oxidized tributylborane could react with *n*-butoxyl radical through SN1 reaction to produce *n*-butyl radical. At the high oxidation degree of tributylborane, more tributylborane was oxidized to peroxylborane, which cleaved to *n*-butoxy radical and borinate radical. So more *n*-butoxy radical was generated, however, the amount of *n*-butyl radical declined due to its diffusion control reaction with oxygen.

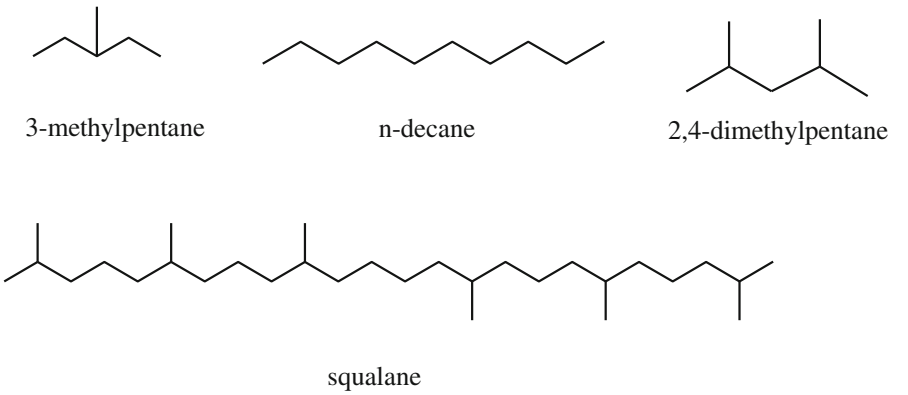
Pathway 1:



Pathway 2:



Scheme 2 Proposed fragmentation pathways of the protonated ions of DMPO/·C_4H_9 adduct



Scheme 3 The structures of alkanes chosen as capturers of *n*-butoxyl radical

The four kinds of alkanes show different C–H bond reactivity to the hydrogen atom abstraction by *n*-butoxy radical. The interplay of a number of potential contributions influences the selectivity towards radical attack at different sites

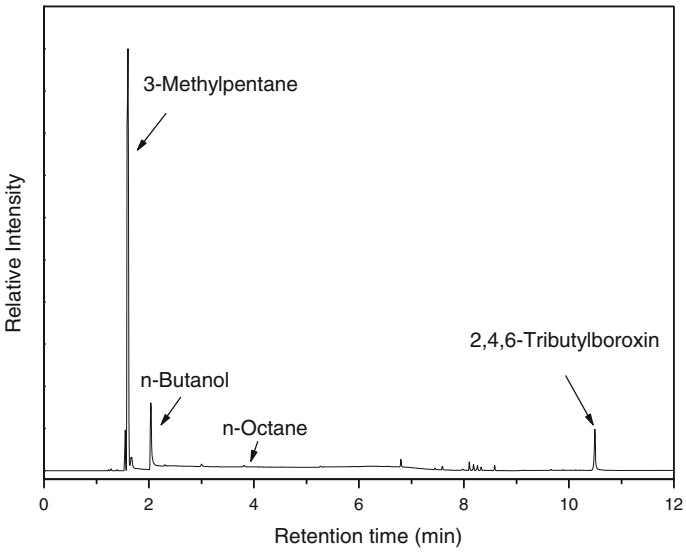


Fig. 4 GC–MS spectrum of the products of 3-methylpentane, TBB, and oxygen

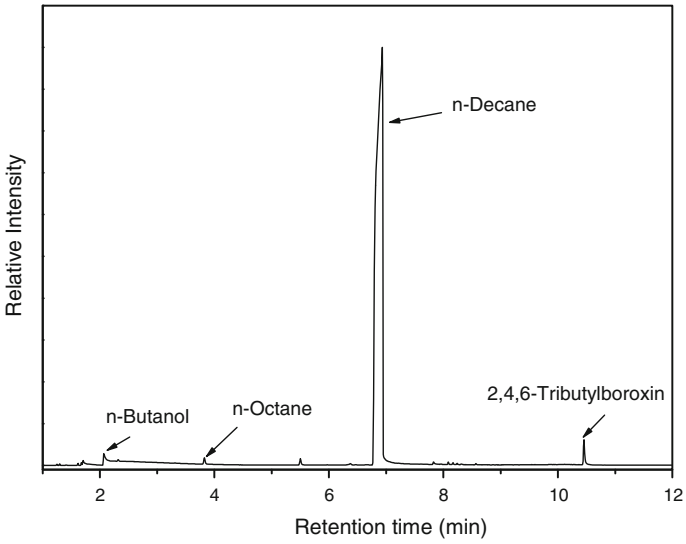


Fig. 5 GC–MS spectrum of the products of *n*-decane, TBB, and oxygen

[21–24]. These include thermochemical effects (radical stability and bond dissociation energy), as well as steric, stereo-electronic, and polar effects. The selectivity of attack on C–H bonds generally follows the expected order tertiary > secondary > primary, correlating with the order of decreasing bond strength. Camara et al. [25] concluded the relative reactivity per hydrogen at 298 K was 3.1 (tertiary):1 (secondary):≫ 1 (primary). However, steric retardation has been

Table 1 Effect of oxygen on the radicals generated from TBB in different models

Model compound	M[a]	*n*-Butanol (%)	*n*-Octane (%)
3-Methylpentane	0.5	39.9	5.2
	1	56.8	7.8
	2	67.7	3.3
	4	71.5	3.0
2,4-Dimethylpentane	0.5	17.2	0.7
	1	25.5	1.1
	4	33.1	0.99
n-Decane	1	1.4	0.3
	4	4.5	0.4
	∞[b]	5.9	0.4
Squalane	0.5	0.5	0.03
	2	0.6	0.04
	4	0.9	0.07
	∞[b]	2.2	–

[a] M was the mole ratio of oxygen to TBB, [b] oxygen was continuously injected

proposed for tertiary and secondary C–H bonds in 2,4-dimethylpentane. Dokolas [26] demonstrated that 2,4-dimethylpentane was three times less reactive than 3-methylpentane towards radical abstraction. For the linear *n*-decane, methylene groups were difficultly attacked by *n*-butoxy radical since they were much less reactive than methine groups at branch alkane. The reactivity of squalane decreased further because of the more steric effect. Therefore, the C–H activity on different alkane decreased in the order 3-methylpentane, 2,4-dimethylpentane, *n*-decane, and squalane.

In the oxidation process of tributylborane, the hydrogen atom abstraction of *n*-butoxy radical from higher active alkanes, such as 3-methylpentane and 2,4-dimethylpentane, would promote the reversible homolytic cleavage reaction of peroxyborane, and produce more radicals (*n*-butoxy and borinate radicals), and then, result in more *n*-butanol. Besides, more *n*-butyl radicals originated from this homolytic cleavage reaction, which coupled with each other in the form of *n*-octane. In the alkanes with inert C–H bond, such as *n*-decane and squalane, the reversible homolytic cleavage reaction of peroxyborane was more favorable to form peroxyborane instead of radicals. As a result, *n*-butoxy radical and *n*-butyl radical were rarely detected.

^{11}B-NMR spectrum was also used to characterize the oxidation products of tributylborane in different alkanes. Various oxidation products could be discriminate without ambiguity [19, 27–29].

Table 2 listed the chemical shifts of detected organoborane compounds. The oxidation products of tributylborane could be categorized into three groups: one form of mono-oxidized tributylborane $Bu_2B(OBu)$; three forms of di-oxidized species, including $BuB(OBu)(OOBu)$, $B_3O_3Bu_3$ and $BuB(OBu)_2$; one form of

Table 2 Chemical shift of tributylborane and tributylborane oxides tested by ^{11}B-NMR

Chemical shift (ppm)	86.8	54.9	35.7	33.1	31.1	18.0
Compound	$B(Bu)_3$	$Bu_2B(OBu)$	BuB(OBu)(OOBu)	$B_3O_3Bu_3$	$BuB(OBu)_2$	$B(OBu)_3$

tri-oxidized tributylborane $B(OBu)_3$. The mono-peroxide tributylborane, $Bu_2B(OOBu)$, was too reactive to be detected.

Figures 6, 7, 8, and 9 were the ^{11}B-NMR spectra, which traced the oxidation process of tributylborane in different alkanes. From the ^{11}B-NMR result, the oxidation process of tributylborane could be deduced as Scheme 4.

In case of deficient oxygen (O_2:TBB<1:1), Bu_3B was first oxidized to $Bu_2B(OOBu)$, which was so vulnerable that it could decompose through homolytic cleavage or react with the residual Bu_3B to form $Bu_2B(OBu)$. With the further increase of oxygen (O_2:TBB>1:1), $Bu_2B(OBu)$ would be subjected to overoxidation to BuB(OBu)(OOBu). Although BuB(OBu)(OOBu) was not as reactive as $Bu_2B(OOBu)$, it could still oxidize $Bu_2B(OBu)$ to $BuB(OBu)_2$, and some of the $BuB(OBu)_2$ tended to be overoxidized to $BuB(OBu)_3$.

Table 3 illustrates the results derived from the above ^{11}B-NMR spectra. It suggested that the oxidizability of tributylborane was affected by different alkanes. In the presence of 3-methylpentane, the hydrogen atom abstraction was beneficial for the homolytic cleavage of $Bu_2B(OOBu)$. Fewer $Bu_2B(OBu)$ could be formed and the oxidizability of tributylborane was enhanced, so that $Bu_2B(OBu)$ was completely oxidized if oxygen was enough (O_2:TBB=1). Meanwhile, more tributylborane was completely oxidized to $B(OBu)_3$. In squalane, the oxidizability

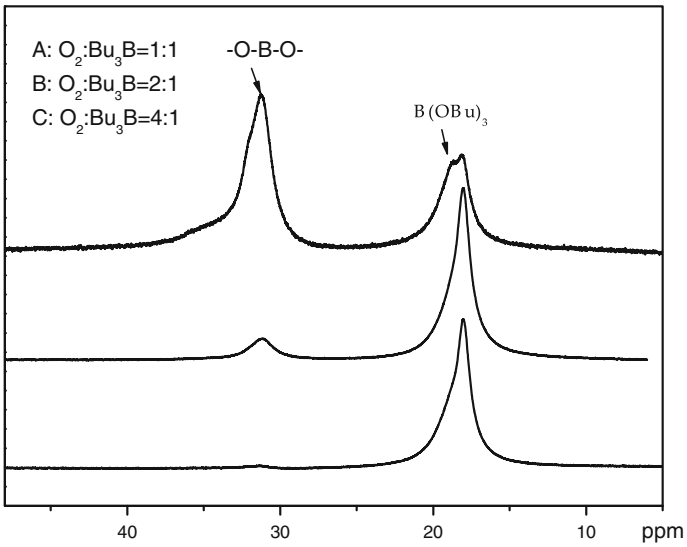


Fig. 6 Effect of oxygen on the ^{11}B-NMR spectra of the mixture of 3-methylpentane and TBB

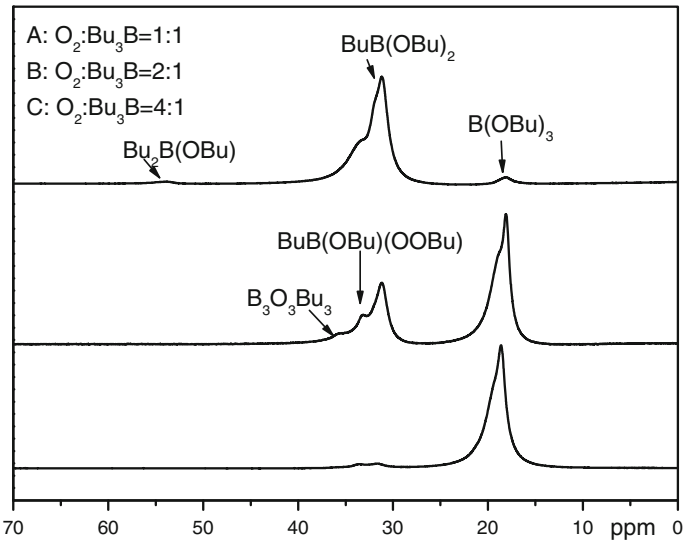


Fig. 7 Effect of oxygen on the ^{11}B-NMR spectra of the mixture of 2,4-dimethylpentane and TBB

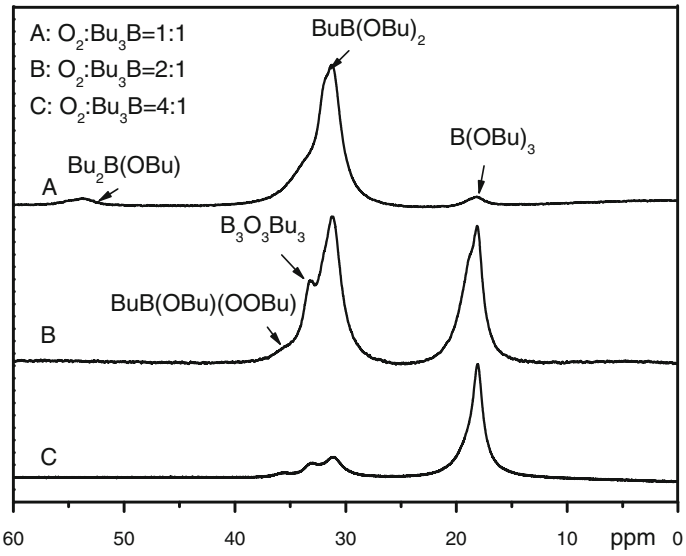


Fig. 8 Effect of oxygen on the ^{11}B-NMR spectra of the mixture of *n*-decane and TBB

of tributylborane decreased tremendously. After the equimolar reaction of tributylborane with oxygen, the remaining $Bu_2B(OBu)$ content was 8.2%. Moreover, tributylborane was not susceptible to complete oxidation. In different models, the oxidizability of tributylborane decreased in the order 3-methylpentane >

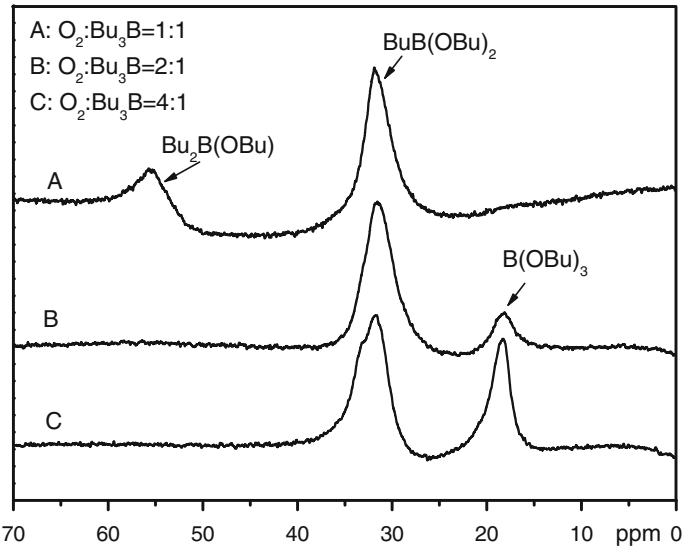


Fig. 9 Effect of oxygen on the ^{11}B-NMR spectra of the mixture of squalane and TBB

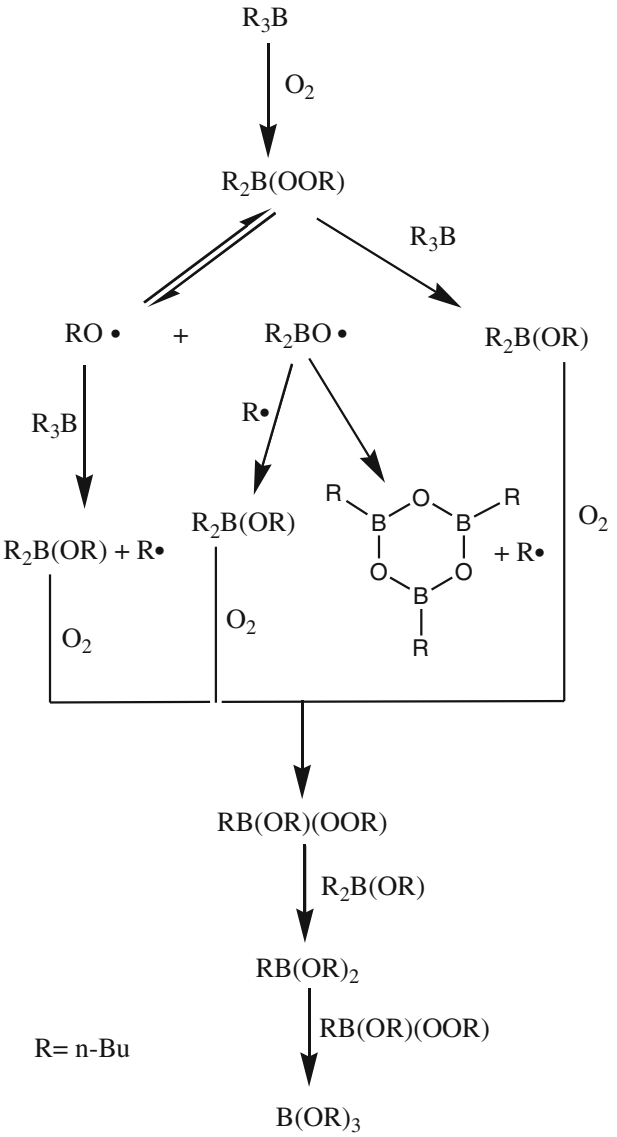
2,4-dimethylpentane > *n*-decane > squalane. It corresponded with the activities of these alkanes toward the hydrogen atom abstraction by *n*-butoxy radicals. The result indicated that the ability of alkane with active C–H bond to capture the radical was beneficial for the oxidizability of tributylborane, which promoted the homolytic cleavage of $Bu_2B(OOBu)$ and the complete oxidation of tributylborane to $B(OBu)_3$. It was the reasons that more radicals were generated when the oxidation of tributylborane proceeded in active alkanes.

2,2-Diphenyl-1-picrylhydrazyl (DPPH) was used as another radical scavenger to evaluate the concentration of radicals. DPPH has an absorption band at 515 nm in its radical form. The absorption intensity decreases after DPPH being scavenged with another active radical, so the final absorption intensity at 515 nm depends on the initial concentration of radicals.

Figure 10 shows that the UV absorption intensity of the mixture of DPPH and tributylborane decreased at 515 nm with the increase of oxygen. This phenomenon suggested that amount of active radicals increased with the increase of oxidation degree of tributylborane. The result was consistent with the above conclusion: the deep oxidation degree of tributylborane was favorable to more generated radicals.

Conclusions

In this paper, the structures of radicals generated in the oxidation process of tributylborane were characterized, and then the oxidation mechanism of trialkylborane was proposed. In the oxidation of tributylborane, three kinds of radicals were found, namely *n*-butoxy, *n*-butyl, and borinate radicals. *N*-butoxy radical was



Scheme 4 The oxidation mechanism of tributylborane

generated from the homolytic cleavage of mono-peroxide tributylborane. The formation of *n*-butyl radical was originated from *n*-butoxy and borinate radicals. The hydrogen atom abstraction by *n*-butoxy played an important role in the oxidation process of tributylborane, which would promote the oxidizability of tributylborane and deepen the oxidation degree of tributylborane, and accordingly, give birth to more radicals.

Table 3 Effect of oxygen on the oxidation of TBB in different alkanes measured by ^{11}B-NMR

Model compound	O_2:TBB (molar ratio)	BBu_3 (%)	$Bu_2B(OBu)$ (%)	–O–B–O– (%)	$B(OBu)_3$ (%)
3-Methylpentane	1	–	–	62.9	37.1
	2	–	–	12.2	87.8
	4	–	–	5.7	94.3
2,4-Dimethylpentane	1	–	0.9	89.8	4.9
	2	–	–	38.9	61.1
	4	–	–	9.2	90.8
n-Decane	1	–	2.7	94.9	2.4
	2	–	–	59.5	40.5
	4	–	–	25.2	74.8
Squalane	1	–	8.2	91.8	–
	2	–	–	85.4	14.6
	4	–	–	65.8	34.2

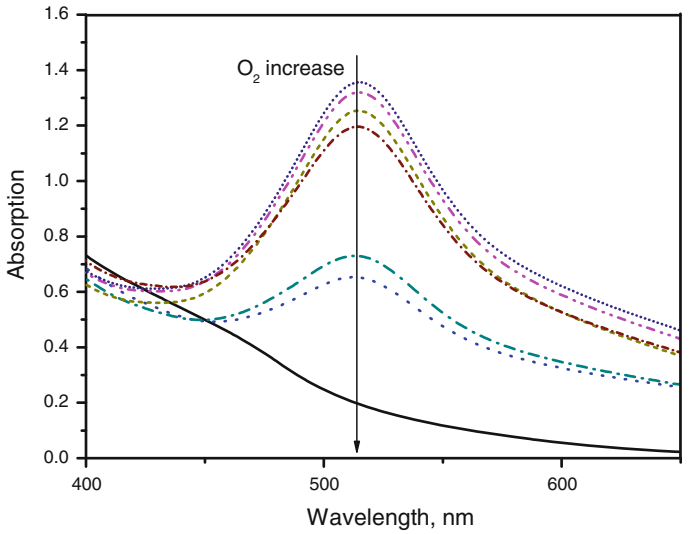


Fig. 10 UV spectra of the mixture of DPPH and TBB solution

References

1. H.C. Brown, M.M. Midland, Angew. Chem. Int. Ed. Engl. **11**, 692 (1972)
2. K.U. Ingold, in *Free Radicals*, vol. 1, ed. by J. Kochi (New York, Wiley 80) (1973)
3. C. Ollivier, P. Renaud, Chem. Rev. **101**, 3415 (2001)
4. J.V. Zharov, J.N. Krasnov, US 5,539,070, (1996)
5. J.L. Kendall, R.F. Righettini, US 6,646,076, (2004)
6. M.F. Sonnenschein, S.P. Webb, N. Rondan, US 6,730,759, (2004)
7. J. Furukawa, T. Tsuruta, T. Imada, H. Fukutani, Die Makromolekulare Chemie **31**, 122 (1959)
8. J. Furukawa, T. Tsuruta, S. Shiotani, J. Polym. Sci. **40**, 237 (1959)

9. K. Noro, H. Kawazura, J. Polym. Sci. **45**, 264 (1960)
10. F.J. Welch, J. Polym. Sci. **61**, 243 (1962)
11. R.L. Hansen, J. Polym. Sci. Part A: Gen. Pap. **2**, 4215 (1964)
12. F.S. Arimoto, J. Polym. Sci., Part A: Polym. Chem. **4**, 275 (1966)
13. Z.M. Wang, H. Hong, T.C. Chung, Macromolecules **38**, 8966 (2005)
14. H. Okamura, A. Sudo, T. Endo, J. Polym. Sci., Part A: Polym. Chem. **47**, 6163 (2009)
15. B. Lu, T.C. Chung, J. Polym. Sci., Part A: Polym. Chem. **38**, 1337 (2000)
16. B. Lu, T.C. Chung, Macromolecules **32**, 2525 (1999)
17. Z.C. Zhang, T.C. Chung, Macromolecules **39**, 5187 (2006)
18. A.G. Davies, Pure Appl. Chem. **39**, 497 (1974)
19. H. Hong, T.C. Chung, Macromolecules **37**, 6260 (2004)
20. Q. Guo, S.Y. Qian, R.P. Mason, J. Am. Soc. Mass Spectrom. **14**, 862 (2003)
21. T. Badel, E. Beyou, V. Bounor-Legaré, Macromol. Symp. **275–276**, 275 (2009)
22. P. Dokolas, M.G. Looney, S. Musgrave, Polymer **41**, 3137 (2000)
23. D. Bertin, S. Grimaldi, P. Tordo, J. Mol. Struct. **811**, 255 (2007)
24. S. Camara, B.C. Gilbert, R.J. Meier, Org. Biomol. Chem. **1**, 1181 (2003)
25. S. Camara, B.C. Gilbert, R.J. Meier, Polymer **47**, 4683 (2006)
26. P. Dokolas, S.M. Loffler, D.H. Solomon, Aust. J. Chem. **51**, 1113 (1998)
27. W.G. Henderson, E.F. Mooney, Ann. Rev. NMR Spectrosc. **2**, 219 (1969)
28. A.R. Siedle, Annu. Rep. NMR Spectrosc. **12**, 177 (1982)
29. A.R. Siedle, Annu. Rep. NMR Spectrosc. **20**, 205 (1988)