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ORIGINAL PAPER

Relating Molecular Structure to Tribological Chemistry: Borate Esters on Copper

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Abstract The surface and tribological chemistry of 2-propanol and borate esters, isopropoxy tetramethyl dioxaborolane (ITDB), and tetramethyl dioxaborolane (TDB) as gas-phase lubricants for copper surfaces are compared by measuring the friction coefficient and contact resistance in an ultrahigh vacuum tribometer. 2-propanol reacts on copper below room temperature to desorb primarily acetone and causes no friction reduction when used as a gas-phase lubricant. TDB decomposes to deposit BO_x species on the surface and produces an initial decrease in friction coefficient that is not sustained. ITDB, which reacts at room temperature to form a tetramethyl dioxaborolide species on the surface, results in an immediate and sustained decrease in friction coefficient when used as a gas-phase lubricant for copper. This indicates that the surface chemistry of the borate esters can be correlated with their tribological properties and illustrates the effect of replacing a hydrogen atom in TDB with a 2-propoxy group in ITDB on both the surface and tribological chemistry. Analysis of the species formed in the wear track after lubrication with ITDB reveals the presence of graphitic or diamond-like carbon and oxygen, and these elements are also found in the subsurface region of the sample. Rubbing the sample in vacuo after reacting with ITDB shows the removal of a boundary film where the coefficient remains constant and the subsequent removal of the subsurface layer in which the contact resistance rises to its original value.

Keywords Borate esters · Copper · Shear-induced surface-bulk transport kinetics · Auger spectroscopy

1 Introduction

The formation of a boundary film by a tribochemical reaction formally proceeds through a sequence of steps that involves adsorption of the additive or gas-phase lubricant on the surface, reaction with the surface, and the formation of a friction and/or wear reducing film, often referred to as a boundary layer or tribofilm. It is generally difficult to identify the initial surface reaction either because of issues with measuring a precise temperature at the tribological interface or because the interfacial temperature is so high that the additives or gas-phase lubricants immediately thermally fragment or decompose into their elements [1]. However, it has recently been shown that surface films can be formed at a copper–copper sliding interface by a shear-induced surface-to-bulk transport mechanism that causes surface adsorbates to be transported into the subsurface region [2–5]. The interfacial temperature rise under the conditions that these experiments are carried out is negligible ($\ll$1 K) [4]. This indicates that the chemistry of the surface precursors formed by reaction with the additives or gas-phase lubricants can be explored and correlated with the nature of the tribofilm that is formed during rubbing. This strategy is illustrated in the following using borate esters on a copper surface.

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Boron-containing compounds provide attractive candidates for environmentally benign lubricant additives since the ester reacts with water to form relatively harmless boric acid [6]. Various boron-containing compounds including borates [7–9], boron nitrides [10, 11], boron carbides [12], and borides [13] exhibit good tribological properties including friction and wear reduction. For example, a borate glass was formed when rubbing iron with trimethylborate as a gas-phase lubricant, which partially digested the iron oxide, but not the metallic iron and led to a significant reduction in friction [9]. However, borate esters tend to hydrolyze quite rapidly and are relatively insoluble in the base oil [14]. They can be rendered less reactive with water by including bridging groups which tend to inhibit the formation of the alcohol product. Alkylated borate esters are more soluble in oil and have been found to have good anti-wear properties [8], and the addition of nitrogen to borates leads to the formation of boron nitride [14].

This work focuses on the surface and tribological reactions of isopropoxy tetramethyl dioxaborolane (ITDB) on copper. This compound (shown in Fig. 1) includes a diolate bridging group to stabilize it against hydrolysis. The surface reaction sequence of ITDB on copper is illustrated in Fig. 1 [15]. The reaction is initiated by B–O bond scission to form 2-propoxy and tetramethyl dioxaborolide species [16–21]. The 2-propoxy group decomposes by both dehydration and dehydrogenation, where dehydrogenation to form acetone predominates. The boron-containing moiety decomposes by evolving acetone. This chemistry contrasts that of tetramethyl dioxaborolane (TDB) where the 2-propoxy group on ITDB is replaced by a hydrogen atom. This substitution results in a drastic modification of the decomposition pathway of the bridging diolate group which now reacts to desorb mainly dimethyl 2-butene. In this case, the room-temperature reaction of TDB with a copper surface is expected to form a BO_x precursor. Consequently, the tribological properties of ITDB and TDB as gas-phase lubricants for copper are compared to establish whether the different surface reaction pathways for two relatively similar borate esters influence their tribological behavior. The experiments are carried out using an ultrahigh vacuum (UHV) tribometer to allow friction to be measured on the same atomically clean copper surface for which the surface chemistry was studied as well as to avoid effects due to atmospheric contamination. These experiments also allow the nature of the surface in the rubbed region to be explored using scanning Auger microscopy to provide post-mortem information on the surface tribochemical reactions.

It should be noted that while differences between the tribological chemistry of ITDB and TDB are to be expected based on their surface chemistry on copper, caution must still be exercised in making direct comparisons; first, the surface will be roughened by rubbing to produce more reactive, low-coordination sites [22] and second, shear at the interface could also cause molecular adsorbates on the surface to decompose.

2 Experimental

Tribological measurements were carried out in a stainless-steel, UHV chamber operating at a base pressure of $\sim 2 \times 10^{-10}$ Torr following bakeout, which has been described in detail elsewhere [23]. Briefly, the chamber was equipped with a UHV-compatible tribometer, which simultaneously measures the normal load, lateral force, and contact resistance between the tip and substrate. Previous work has demonstrated that the maximum interfacial temperature rise for a copper sample under the experimental conditions (4×10^{-3} m/s sliding velocity, 0.5 N normal load) is much less than 1 K [4]. All experiments were carried out by initially rubbing the spherical tribopin (of 1.27×10^{-2} m in

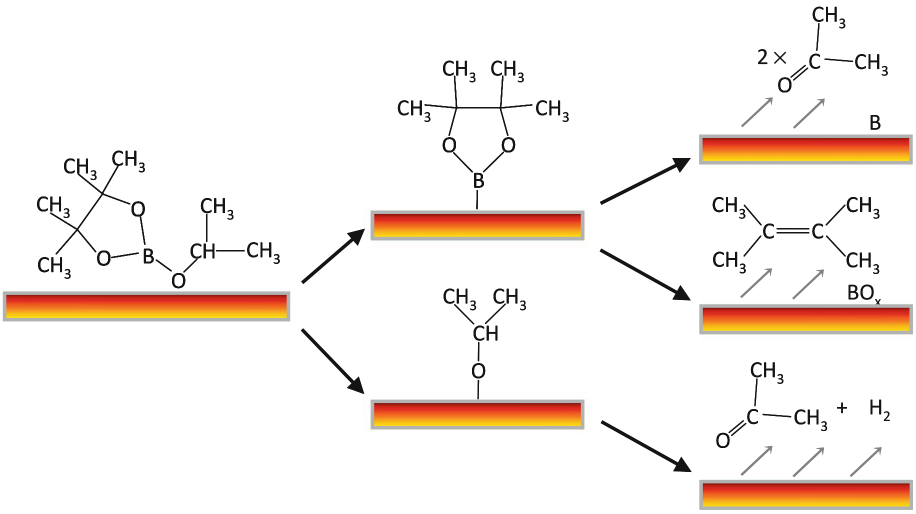

Fig. 1 A schematic diagram showing the reaction sequence found for isopropoxy tetramethyl dioxaborolane (ITDB) on a copper surface

diameter, made from tungsten carbide containing some cobalt binder) against the clean copper sample until a constant friction coefficient was obtained, a process that usually required ~ 50 scans. This formed a wear track on the surface, likely resulting in the transfer of copper to the tribopin, so that friction results are for a sliding copper–copper interface. The reactants were dosed through a leak valve connected to a dosing tube (with an internal diameter of 4×10^{-3} m) directed toward the sample so that the pressure at the sample is enhanced compared to the measured background pressure. The chamber also contained a single-pass, cylindrical-mirror analyzer (CMA) for Auger analysis and an argon ion bombardment source for sample cleaning and depth profiling. A high-resolution electron gun with a beam energy of 5 kV and a channeltron secondary electron detector were also incorporated into the system. This allowed scanning electron microscopy (SEM) images and Auger profiles of the wear scars to be collected. Finally, the chamber also included a quadrupole mass spectrometer for leak checking and for gauging reactant purity.

The copper samples (Alfa Aesar, 99.99 % pure, 1-mm thick) were polished to a mirror finish using 1 μm diamond paste, then rinsed with deionized water and ultrasonically degreased in acetone. Once in UHV, the copper foils were cleaned using a standard procedure which consisted of Argon ion bombardment (~1 kV, ~2 μA/cm^2) and annealing cycles up to ~850 K. The cleanliness of the samples was monitored using Auger spectroscopy.

Friction coefficients of borate esters dissolved in a poly α-olefin (PAO) were also measured using a pin and V-block apparatus as described in detail elsewhere [24, 25] to allow the results, measured in UHV, to be compared with those collected for the borate esters in solution.

The ITDB (Aldrich, 98 % purity), 2-propanol (Aldrich, 99.5 % purity), and TDB (Aldrich, 97 % purity) were transferred to glass bottles and attached to the gas-handling systems of the vacuum chambers, where they were subjected to several freeze–pump–thaw cycles. The purities of the compounds were monitored using mass spectroscopy.

3 Results

The gas-phase lubrication of a copper sliding contact by the borate esters (ITDB and TDB) and 2-propanol was compared in a UHV tribometer. Typical results, in this case for ITDB, are displayed in Fig. 2. The tribopin was initially rubbed against the clean copper surface until no change in friction occurred, resulting in the formation of a wear track on the surface. This insured that any subsequent changes in friction coefficient were caused by gas-phase lubrication and not by any evolution of the contact properties. The surface was then exposed to ITDB (at a background dosing pressure of 3×10^{-8} Torr) and the friction coefficient and contact resistance were simultaneously monitored for each rubbing cycle. In the following, the results are plotted versus the number of scans after the completion of the run-in period. Experiments were carried out at loads of 0.44 N (Fig. 2a) and 0.88 N (Fig. 2b). In both cases, the friction coefficient (filled square) drops rapidly from an initial value of ~0.5 to ~0.32 when the normal load is 0.44 N, and to an almost identical value of ~0.33 when the load is 0.88 N. It was also observed that while the friction coefficient drops almost immediately when the surface is dosed with ITDB, the contact resistance (open square) rises slowly and almost linearly with the number of rubbing cycles. Thus, the contact resistance measurements provide an in situ indication of how the tribofilm is evolving during reaction with the gas-phase lubricant.

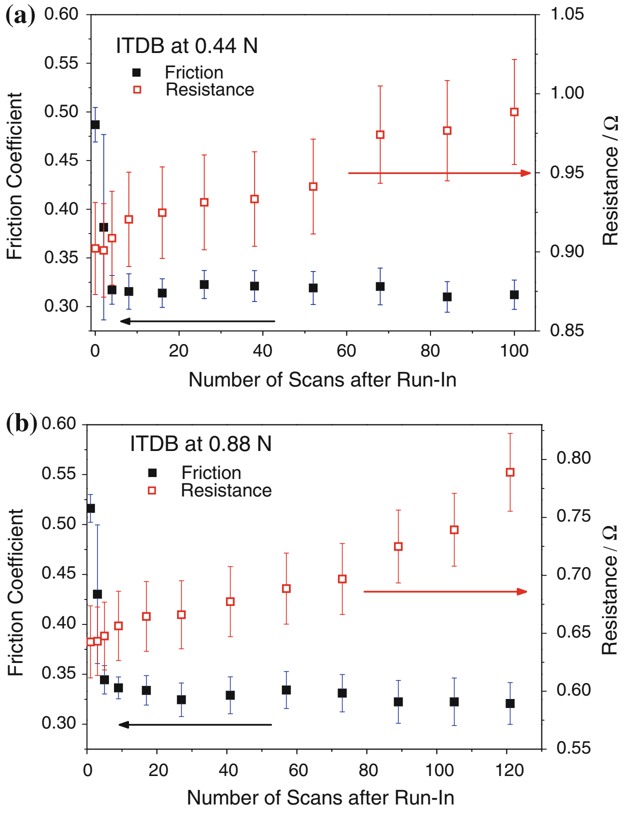

Fig. 2 Plots of friction coefficient (*filled square*) and contact resistance (*open square*) measured as a function of the number of rubbing cycles while dosing copper with isopropoxy tetramethyl dioxaborolane (ITDB) at a background pressure of 3×10^{-8} Torr, a sliding speed of 1×10^{-3} m/s, and a normal load of **a** 0.44 and **b** 0.88 N

The tribological properties of the different gas-phase lubricants are compared in Fig. 3 when the molecules were dosed using a background pressure of 3×10^{-8} Torr and the data were collected using a normal load of 0.44 N. As emphasized above, the gas-phase molecules effuse from a dosing tube that is incident on the surface so that the local

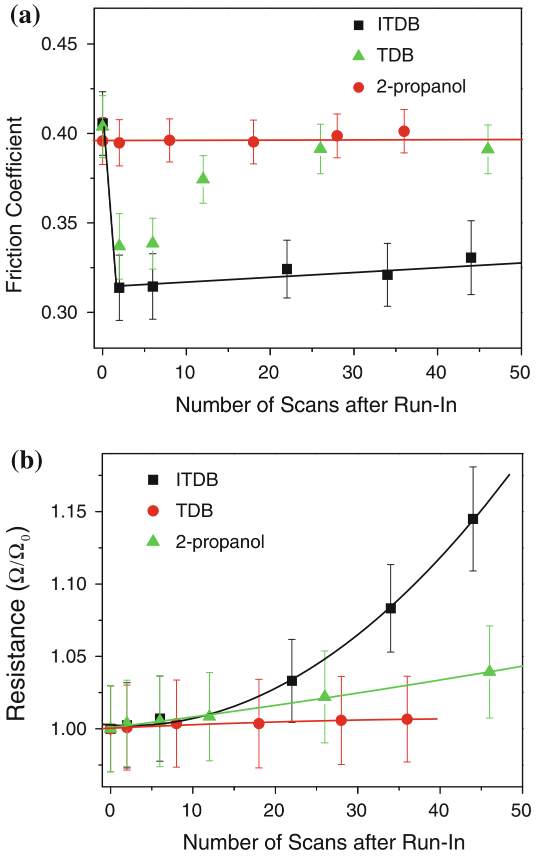

Fig. 3 Plots comparing the friction coefficient **a** and relative contact resistance **b** as a function of the number of rubbing cycles when dosing copper using a background pressure of 3×10^{-8} Torr of isopropoxy tetramethyl dioxaborolane (ITDB, *filled square*), tetramethyl dioxaborolane (TDB, *filled triangle*), and 2-propanol (*filled circle*) with a normal load of 0.44 N at a sliding speed of 5×10^{-3} m/s

pressure at the sample will be higher than the measured background pressure. The results in Fig. 3 reveal that each of the molecules has drastically different tribological behavior. 2-propanol (filled circle) causes no decrease in friction with dosing and rubbing (Fig. 3a). Figure 3b plots the normalized resistance (Ω/Ω_0), where Ω_0 is the initial contact resistance, as a function of the number of passes and lines are plotted through the data as a guide to the eye. Dosing copper with 2-propanol (filled circle) causes no discernible change in contact resistance. This suggests, but does not prove, that no tribofilm is being formed since it could conceivably be that a film still forms without changing the conductivity of the system. However, it is unlikely that the tribofilm is as conductive as copper and, taken together with the lack of change in friction, strongly indicates that the 2-propanol does not react to form a tribofilm under these conditions.

In contrast, a modest initial friction decrease is found when using TDB (Fig. 3a, filled triangle), but the friction coefficient starts to rise once again after ∼6 scans and by 20 scans, it has returned to the initial value for rubbing against the clean surface. This is in accord with the contact resistance results (Fig. 3b, filled triangle) which show a very modest increase (of ∼3 %). Apparently only a very thin tribofilm is formed by exposure to TDB that appears to be removed from the surface as rubbing proceeds. In contrast, ITDB shows a substantial decrease in friction (Fig. 3a, filled square), which initially decreases to a slightly lower value than the initial friction coefficient found when using TDB, confirming the results shown in Fig. 2. However, in this case, the friction coefficient maintains this constant low value as the surface is rubbed (Figs. 2, 3a) and the contact resistance continues to increase as the number of passes increases (Figs. 2, 3b). Clearly, in spite of their structural similarities, ITDB and TDB show significantly different tribological behavior.

In order to explore the nature of the tribofilm in greater detail, the evolution in friction coefficient and contact resistance was monitored after the initial tribofilm was formed using ITDB by continuing to rub after stopping dosing the surface. ITDB was selected for this experiment since 2-propanol shows no tribochemical activity, and the friction coefficient when using TDB rapidly rises back to its initial value while dosing; also, the contact resistance changes in these cases are small so that its evolution would be difficult to follow after dosing had ceased. A typical result is shown in Fig. 4. The experiments were carried out at a normal load of 0.25 N and an ITDB dosing pressure of 3×10^{-8} Torr. A slightly lower normal load was used for these experiments in order to attempt to extend the wear period to allow more detailed measurements to be made. In each case, the tribofilm was formed for some number of

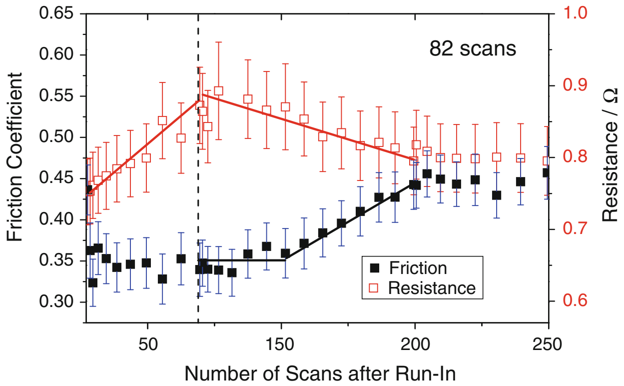

Fig. 4 Typical plot of friction coefficient (*filled square*) and contact resistance (*open square*) measured as a function of the number of rubbing cycles at a normal load of 0.25 N, while dosing the copper sample with a background pressure of 3×10^{-8} Torr of isopropoxy tetramethyl dioxaborolane (ITDB). The sample was rubbed while dosing for 82 scans at which point the isopropoxy tetramethyl dioxaborolane (ITDB) dosing was ceased (indicated by a *vertical dotted line*), while the friction coefficient and contact resistance were measured

passes while dosing (12, 41, 82, and 153 passes, and the typical results for 82 passes are displayed in Fig. 4). The friction coefficient and contact resistance are shown plotted after completing the run-in period (of ~50 scans) and just before dosing ITDB. In all cases, the initial drop in friction coefficient with number of scans is identical (yielding a value of ~0.35) and remains rather constant thereafter as long as the sample is being dosed with ITDB (filled square), while the contact resistance increases (open square). This is in accord with the results shown in Figs. 2 and 3. After ITDB dosing had ceased (indicated by a vertical, dotted line), two phases in the subsequent behavior of the friction coefficient and contact resistance can be discerned. In the first phase, the friction coefficient remains constant for some number of scans in spite of the ITDB dose having been turned off, and the contact resistance starts to decrease. This effect is not due to the time required for the ITDB pressure to decrease, first because the pump used in the UHV chamber is sufficiently large that the pressure drops quite rapidly. Second, the number of scans over which the friction coefficient is constant varies with the initial dosing time, while the dosing pressure was identical for all experiments. Finally, the contact resistance decreases, while it would continue to increase in the presence of ITDB.

After the completion of this initial, constant-friction-coefficient phase, the friction coefficient starts to rise back to its initial value. This is accompanied by a continued decrease in contact resistance. The number of scans for which the friction coefficient remains constant after the ITDB beam has been turned off is plotted versus the number of scans while dosing (Fig. 5, filled square), clearly showing a linear dependence with a slope of 0.9 ± 0.1. Shown also in this figure is the number of scans needed for the friction coefficient to rise to its original value after dosing plotted versus the number of scans while dosing ITDB (filled circle), which shows a similar linear behavior with a slope of 1.6 ± 0.1.

To provide insight into the composition of the surface and subsurface of the sample, the wear scar and unrubbed surface were analyzed using spatially resolved Auger spectroscopy and the results are displayed in Fig. 6. The Cu Auger (LMM) peaks are evident in all spectra between ~750 and 910 eV kinetic energy (KE). Within the wear track (top spectrum), an intense C KLL Auger signal is detected at ~270 eV KE and some oxygen is observed at ~520 eV KE. The relative proportion of boron in ITDB is rather low so that any boron-derived Auger features are expected to be weak. A boride would display a boron Auger KVV peak at ~185 eV KE [26]. This is marked on the spectrum and there is no discernible feature at this energy. B_2O_3 has a KVV Auger feature at ~172 eV, where the shift arises since the Auger transition involves the valance levels of boron [26]. However, while there may be some evidence of small features within this energy range, they are not sufficiently intense to unequivocally state that boron is detected by Auger spectroscopy.

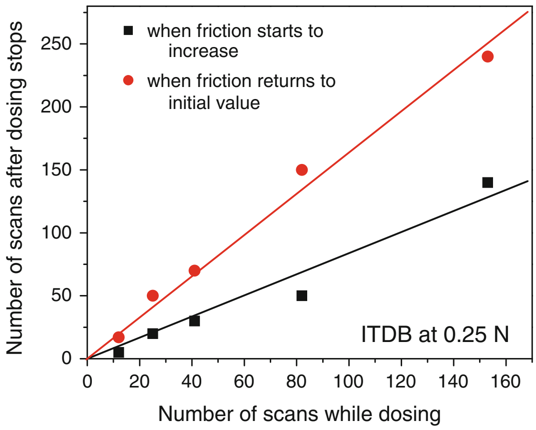

Fig. 5 Plot of the number of scans for which the friction coefficient remains constant after the isopropoxy tetramethyl dioxaborolane (ITDB) beam has been turned off (*filled square*) and the number of scans needed for the friction coefficient to rise to its original value after dosing, both plotted versus the number of scans after the completion of the initial run-in period (*filled circle*)

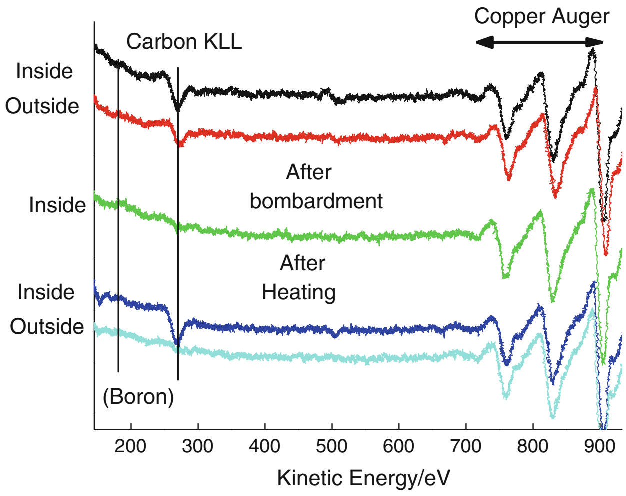

Fig. 6 Auger spectra collected after dosing the copper sample with isopropoxy tetramethyl dioxaborolane (ITDB) at a background pressure of 3 × 10^{-8} Torr using a normal load of 0.44 N at a sliding speed of 5 × 10^{-3} m/s, inside and outside the wear track (top two spectra). The surface was then Argon ion bombarded to remove the surface species resulting in the middle Auger spectrum. After heating to 780 K, the bottom Auger spectra were obtained inside and outside the wear track

Similar Auger features are detected outside the wear track, but with much lower intensity than inside. The shape of the carbon KLL Auger signal can provide some information on the nature of the carbonaceous species, in particular from the energy spacing between the main KLL

Auger transition (given by the energy at the minimum in the negative excursion of the peak) and the low-energy satellite (given by the maximum in the positive excursion). In graphite or diamond-like carbon, the spacing is ~22 eV [27], while in transition-metal carbides it is much less [28]. The spacing in the spectrum in Fig. 6 (of ~22 eV) indicates that carbides have not formed and that the carbon feature resembles that of graphite or diamond-like carbon [29]. The surface was then bombarded with Argon ions to remove all surface species to identify the composition of the subsurface using a strategy described in detail elsewhere [2, 3]. In this case, subsequently heating the sample will result in species that have penetrated the subsurface region while rubbing to diffuse once again to the surface and be detected by Auger spectroscopy. The results of this experiment are shown in the bottom two spectra in Fig. 6. No additional signals are detected outside the wear scar since the temperature is too low for adsorbates to have thermally diffused into the bulk. In contrast, both carbon (KLL signal at ~280 eV KE) and oxygen (KLL signal at ~520 eV KE) are detected once again.

Finally, in order to establish whether the frictional properties when using ITDB, TDB, and 2-propanol as gas-phase lubricants in UHV correlate with their behavior as lubricant additives, the friction coefficients of 5 wt % solutions of TDB, ITDB, and 2-propanol dissolved in a poly α-olefin (PAO) were measured using a pin and V-block apparatus [24, 25]. The resulting values are compared with the friction drops found in UHV in Table 1. Here, the differences in friction coefficient for the two dioxaboralane derivatives correlate with the initial and final decreases in friction coefficient of these two compounds measured in the UHV tribometer, while adding 2-propanol has no effect on the friction coefficient compared to PAO alone. This suggests that the model studies in UHV are relevant to the processes occurring in a more realistic environment.

4 Discussion

The tribological behavior of 2-propanol, TDB, and ITDB correlates with the surface chemistry of these molecules identified in UHV [15]. Adsorbed 2-propanol dehydrates on copper below room temperature, while 2-propoxy species formed on the surface start to undergo β-hydride elimination at a little below 300 K. Thus, dosing copper with 2-propanol at 300 K, assuming that the chemistry on the rougher surface formed in the wear track is similar to that on clean copper, would form 2-propoxy species that would react to desorb acetone and thus not be expected to reduce friction or form a tribofilm in accord with the results displayed in Fig. 3.

When ITDB reacts on copper, some dimethyl 2-butene is formed at ~364 K, and acetone is found to desorb starting just below 300 K due to decomposition of the 2-propoxy group in ITDB, while additional acetone desorbs at ~391 K [15]. Thus, at 300 K, again assuming that the surface chemistry in the wear track resembles that found on clean copper, two species are initially formed on the surface and are shown in Fig. 1. As noted above, the 2-propoxy species desorb and do not contribute to tribofilm formation, so that any friction reduction must be due to the presence of the tetramethyl dioxaborolane-like species that are stable up to 360–390 K, well above the interfacial temperature attained during sliding in the UHV tribometer.

TDB decomposes via a completely different pathway compared to ITDB, so that the presence of the 2-propoxy group in the borate ester has a profound effect on the surface chemistry. TDB reacts to desorb dimethyl 2-butene at somewhat below room temperature to leave BO_x species on the surface. Thus, under the conditions at which the tribological measurements are carried out, BO_x species are likely to be present. This appears to cause some initial reduction in friction once sliding starts, but is worn from the surface sufficiently rapidly that this friction reduction is not sustained (Fig. 3; Table 1).

The stoichiometry of the intermediate formed from ITDB by the surface chemistry [15] is $C_6H_{12}O_2B$ (Fig. 1). Hydrogen is not detectable by Auger spectroscopy, but the relative peak-to-peak intensities of the C and O KLL Auger features outside the wear track (6 ± 1) are consistent with this stoichiometry [30]. The C:O Auger ratio inside the wear track is very close to this value (5.5 ± 1.0), suggesting that the composition within the wear track is dictated by the composition of the precursor. The relative

Table 1 The initial and long-term friction coefficient decrease measured in a UHV tribometer for 2-propanol, ITDB, and TDB compared with the friction coefficient for 5 wt % of these molecules dissolved in PAO measured in a pin and V-block apparatus

	Ultrahigh vacuum measurements		Pin and V-block measurements
Additive	Initial friction drop, $\Delta\mu$ (initial)	Long-term friction drop, $\Delta\mu$ (long-term)	Friction coefficient (μ)
2-Propanol	0	0	0.40 ± 0.05
ITDB	0.18 ± 0.02	0.18 ± 0.02	0.18 ± 0.02
TDB	0.07 ± 0.02	0	0.30 ± 0.06

Auger sensitivities of boron and oxygen [30] indicate that, for a surface with a B:O ratio of 1:2, the boron Auger signal should be ~50 % of the oxygen signal, thereby rationalizing the absence of a clear boron Auger signal on the surface (Fig. 6).

Thus, the presence of a 2-propoxy species in the ITDB functions as a reactive group by undergoing B–O bond scission to deposit a stable boron-containing moiety. In addition to stabilizing the borate ester against hydrolysis, the bridging group in ITDB also serves to stabilize a molecular fragment on the surface.

The surface ITDB-derived species is likely to decompose at the shearing interface, although little is known about this process. The resulting Auger features inside the wear track are more intense than those outside, while their relative intensities are consistent with the carbon and oxygen contents in the precursor borate ester. A similar increase in coverage inside the wear track has been noted when using dimethyl disulfide as a gas-phase lubricant [3, 4] and has been ascribed to the presence of an atomically rougher surface that can accommodate a higher adsorbate coverage.

Previous experiments have explored the shear-induced surface-to-bulk transport of the surface thiolate species formed from dimethyl disulfide (DMDS) on copper [2–4] where continually dosing the surface with DMDS, while rubbing results in a reduction in friction coefficient. Interfacial shear results in sulfur being transported into the subsurface region where it penetrates ~0.7 nm per scan at a normal load of 0.44 N [5]. In this case, it was found that the distribution of sulfur in the subsurface region reached a constant value after ~130 scans, so that the surface-to-bulk transport kinetics were found to be self-limiting. This was ascribed either to a change in the shear properties of the copper caused by the presence of sulfur or to the formation of a boundary film that localized the shear. Thus, the film formed on the surface by dosing a copper sample with DMDS, while scanning comprises a sulfur-rich surface layer formed by DMDS decomposing on the surface, a subsurface region which contains some sulfur and carbon formed by the shearing interface, with clean copper below.

The structure of the films formed from ITDB is explored both by Auger analysis of the wear scar (Fig. 6) and by measuring the friction coefficient and contact resistance after having stopped reaction with ITDB (Fig. 4). It appears that an analogous film structure forms when using ITDB. Here, the initial thermal reaction forms a tetramethyl dioxaborolane-like species on the surface (Fig. 1), distinct from the BO_x species formed from TDB. Shear appears to cause the molecular species to decompose into its elements and then be transported into the subsurface region, thereby producing an analogous film structure with a surface layer containing primarily graphitic or diamond-like carbon and a subsurface layer that also comprises carbon and oxygen that are transported into the subsurface region by interfacial shear.

The film structure is explored by measuring the friction coefficient and contact resistance of the sample after ITDB dosing had ceased. This is expected to remove the surface layers (either by wear or by shear-induced transport into the substrate), and the subsequent evolution of friction and contact resistance after stopping the gas-phase lubricant occurs in two distinct phases (Fig. 4). Initially, the friction coefficient remains constant and the contact resistance Ω decreases, and the number of scans to complete this phase is proportional to the number of times the surface was rubbed in the presence of ITDB, with a proportionality constant of 0.9 ± 0.1 (Fig. 5). Subsequently, the friction coefficient slowly rises to its original value, while the contact resistance continues to decrease, where the number of scans to complete this phase is also proportional to the number of scans over which this phase was formed in the presence of ITDB, with a proportionality constant of 1.6 ± 0.1 (Fig. 5). Based on the results of experiments carried out using DMDS [3–5], this suggests that the first phase is associated with the gradual loss of the surface comprising graphitic carbon (Fig. 6). The wear rate is not known, but assuming that it is reasonably constant, the results of Fig. 5 suggest that the thickness of this film increases with dosing time and that its friction coefficient is independent of thickness. This implies that shear is localized toward the outside of the film and this result is in accord with the initial rapid decrease in friction when the film is initially dosed (Figs. 2, 4). Once the surface film has been removed (and/or been transported into the subsurface region), friction increases as sliding occurs against the subsurface layer. However, when the sulfur-containing additive DMDS was used, the distribution of the sulfur in the subsurface region was found to be identical for 130 and 366 scans [5]. If a similar phenomenon occurred when using ITDB, it would be expected that the plot of the total number of scans needed to remove the film as a function of the number of scans required to form it would reach a plateau at the number of scans at which the shear-induced surface-to-bulk transport ceased. This has not occurred up to the total number of scans used in this experiment (~160).

Finally, the friction coefficient found when using TDB and ITDB as lubricant additives to PAO correlates well with the friction drop for gas-phase lubrication measured in UHV (Table 1), and no change in friction was found with 2-propanol. This implies that the surface chemistry and surface-to-bulk transport process found by surface-science strategies and UHV tribometry can provide insight into the processes occurring under more realistic tribological conditions.

5 Conclusions

The surface chemistry of 2-propanol, TDB, and ITDB on copper was correlated with the tribological properties of these molecules used as gas-phase lubricants, measured in UHV. 2-Propanol completely decomposes below room temperature and therefore causes no reduction in friction, while TDB reacts to form BO_x species which causes some initial friction reduction, which is not sustained. Replacing the hydrogen in TDB with a 2-propoxy group to form ITDB has a profound effect on both the surface and tribological chemistry, and ITDB initially reacts to form a tetramethyl dioxaborolane-like species and results in a rapid and sustained reduction in the friction coefficient of copper when used as a gas-phase lubricant. An analysis of the wear track after rubbing reveals the presence of carbon and oxygen, where the carbon is present as graphite or diamond-like carbon, as well as revealing the presence of these elements below the surface. A wear depth profile reveals the presence of two regimes. In the first, the friction coefficient remains constant, while the contact resistance decreases and is ascribed to the removal of a surface boundary film. The time required to remove this film is proportional to the time taken to form it. In the second regime, the friction coefficient rises to the original value measured for sliding against the clean copper surface and is also accompanied by a decrease in contact resistance and is ascribed to the removal of material that had been transported below the surface due to interfacial shear. Again, the time taken to remove this subsurface film is proportional to the time required to form it.

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