of either the $CuCl_2^-$ or $CuCl_3^{2-}$ species to change the fact that at the irradiating wavelength of 274 nm the only absorbing species is $CuCl_3^{2-}$, and thus our original observation of the drop in quantum yield with increasing temperature is still valid.

Registry No. $CuCl_2^-$, 15697-16-2; $CuCl_3^{2-}$, 29931-61-1; Cl^-, 16887-00-6.


Contribution from the Department of Chemistry, Cornell University, Ithaca, New York 14853

Disproportionation of Dimethoxyborane

Peter M. Jeffers* and S. H. Bauer

Recently we reported[1] on the partial reduction, in the gas phase, of trimethoxyborane by hydrogen, effected by flowing mixtures of the gases through a low-power microwave discharge. Here we describe tests conducted to confirm the occurrence of the disproportionation reaction

$$6HB(OCH_3)_2 \rightleftharpoons B_2H_6 + 4B(OCH_3)_3 \qquad (1)$$
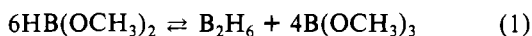
This route for the production of diborane was discovered by Burg and Schlesinger in 1933;[2] the gas-phase kinetics were studied by Uchida et al.[3] That it takes place in the liquid phase was reported by the latter authors in 1956.[4] From thermochemical data summarized by Dewar and McKee[5] it follows that in the gas phase, for reaction 1, $\Delta H°_{300} \approx -22$ kcal/mol. We estimated $\Delta S°_{300} \approx -30$ eu. Hence K_{eq}^{300} $(atm^{-1}) \approx 3 \times 10^9$. The disproportionation would go almost to completion were it not rate limited.

Concurrently we extended our previous investigations to determine the magnitude of the experimental parameters for our small generator so as to optimize the yield of the dimethoxy compound and to minimize the loss of boron bearing species.

Brief Test on the Liquid Phase. A continuous-flow system with three parallel microwave discharge paths was constructed. The three streams were combined, and the flow was directed through a trap at -78 °C (to remove the methanol); the volatile products were condensed in a liquid-nitrogen (LN) trap. The accumulated material from a 2-h run was then brought up to -120 °C, degassed at that temperature, and then raised to -78 °C, from which it was distilled into a freshly cleaned Pyrex bulb (chromic acid, distilled water–acetone) at LN temperature. When the sample was warmed to 20 °C not all of the liquid had vaporized. The presence of some liquid proved essential. After 20 h of remaining at room temperature, B_2H_6 was demonstrated to be present, by both IR and mass spectral analysis. The conversion was incomplete; the material in the gas phase had the ratio $HB(OCH_3)_2/B(OCH_3)_3 > 1$. We consider this to be essentially a confirmation of the 1956 reports,[4] in contrast to our attempts to reproduce the gas-phase kinetics data published in 1959.

Disproportionation (?) in the Gas Phase. (i) All our attempts to establish reaction 1 in reactors which duplicated *as closely as possible* the experimental configuration described by Uchida[3] were negative. These are detailed below. The combined streams from the three microwave tubes entered a 20 cm long tube (2-cm diameter), packed either with glass wool or with 2–4-mm chuncks of graphite. The reactor was wrapped with heating tape for temperature control, and the catalysts were degassed. The outflow was directed into two traps fitted with cold fingers and sampling ports. No B_2H_6 could be detected in the traps or effluents for reactor temperatures 20–120 °C.

The $HB(OCH_3)_2$ from the microwave tubes was trapped at -120 °C after being passed through a -78 °C trap to remove most of the CH_3OH. Various portions of the dimethoxy compound were fed through the reactor, which had either glass wool or graphite chuncks, for periods from 5 min to 15 h at temperatures ranging from 20 to 95 °C; no B_2H_6 was generated. The products always were $B(OCH_3)_3$ and H_2, in addition to white deposits (B_2O_3?) which appeared in the traps and on the glass wool.

(ii) We tested the "uncatalyzed" reaction as follows. A 250-mL Pyrex flask was thoroughly cleaned with chromic acid, distilled water, and acetone, attached to a mercury manometer, and wound with a heating tape. The bulb was thoroughly evacuated under extended heating, filled with a mixture which consisted of 70% $HB(OCH_3)_2$ and 30% $B(OCH_3)_3$ to a total pressure of 14.5 torr, and allowed to remain at 20 °C for 23 h. No change in pressure was noted. To this flask was added an additional sample of approximately 40% $HB(OCH_3)_2$ to a total pressure of 136 torr and warmed to 60 °C for 20 h and then to 80 °C for an additional 20 h. No significant change in pressure was noted. Were equilibrium attained, we would have observed a pressure decrement of 9.3 torr. We concluded that in a *clean* vessel the rate for reaction 1 in the gas phase was so slow as to be insignificant at 80 °C.

(iii) Concurrently a portion of the 70% material was kept in an infrared cell (40-cm^3 volume) at a pressure of 12 torr. After 23 h at room temperature, the infrared spectrum showed that almost all the dimethoxy compound had decomposed. Only trimethoxyborane and hydrogen were present in the gas phase, as demonstrated by mass spectral analysis. We concluded that decomposition of the dimethoxyborane occurred heterogeneously on silica (and possibly NaCl) surfaces which had not been thoroughly cleaned. However, the reaction products did not produce B_2H_6.

Careful reading of the two papers in which reaction 1 was presumed to have occurred in the gas phase showed that no direct demonstration of the presence of diborane was made by either group of investigators. All the analytical conclusions were based on the magnitudes of the residual pressure of gas left after removal of the di- and trimethoxyboranes. Our experiments indicate that this gas was hydrogen, which may have resulted from the reaction of the dimethoxy compound with moisture adsorbed on the glass walls or possibly with OH from hydrated silica or with methyl alcohol which evaded the -78 °C trap. Uchida et al.[3] reported reaction 1 to be second order and heterogeneous, efficiently catalyzed by charcoal. They presented rate data for 40, 60, and 80 °C. Although our experiments were conducted at pressures $^1/_3$ and $^1/_{30}$ those of Uchida's, the sensitivity of the analysis for B_2H_6 should have yielded a detectable absorption band if in fact reaction 1 had occurred at the rates reported by these authors.

Optimized Conditions for Dimethoxyborane Production. In the three-stream microwave generator, the flows of hydrogen

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(2) Burg, A. B.; Schlesinger, H. I. *J. Am. Chem. Soc.* **1933,** *55,* 4020.
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and trimethoxyborane were precisely controlled by metering valves and measured with a calibrated flow meter. The vapor pressure of $B(OCH_3)_3$ at room temperature was sufficient to provide the desired flow from a reservoir of the liquid. The microwave coupling heads could be positioned along $^1/_2$-in. o.d. Pyrex tubes from 2 to 20 cm upstream from the quenching traps. However, use of the quenching traps (from room temperature to −20 °C) did not significantly enhance the yield of the dimethoxy compound for any position of the discharge head. (The traps were eventually removed.) Cleanliness of the discharge tubes was an important constraint—contamination by dioctyl phthalate from the flow meters led to poor conversions. Some decomposition of the trimethoxy compound also occurred, and the yield of the dimethoxy species dropped drastically when a perceptible white deposit (B_2O_3) built up in the discharge region. The optimum flow conditions were about 5% of the trimethoxyborane in hydrogen, at a total pressure of 7–12 torr, with a linear flow rate of about 2–10 m/min. Increasing the flow rate to 20 m/min, even with the percent of $B(OCH_3)_3$ halved, and at the same total pressure, led to rather poor fractional conversions, indicating that the residence time is an important constraint. Mixtures of less than 5% $B(OCH_3)$ in H_2 gave good fractional yields, but above 5%, conversion dropped significantly. Our most successful runs ranged from 45 to 75% conversion to $HB(OCH_3)_2$, with little side products; the trimethoxy compound could be readily recovered. In all cases the microwave power was about 10–20 W/head; higher powers caused significant decomposition and production of large amounts of acetylene.

Production yields under our nearly optimum conditions—for three parallel streams—were as follows (μW power used $\lesssim$30 W): $B(OCH_3)_3$ processed, 1.1×10^{-3} g/min; H_2 processed, 2.1×10^{-3} g/min; $HB(OCH_3)_2$ produced, 6.6×10^{-4} g/min; $B(OCH_3)_3$ recovered, $\sim 3 \times 10^{-4}$ g/min. No IR absorptions nor mass spectra were detected for $B_2(OCH_3)_4$.


Contribution from the Department of Chemistry, University of New Mexico, Albuquerque, New Mexico 87131

Crystal and Molecular Structure of Sodium Hydrogen Bis(μ-*ms*-tartrato)-bis(2,2′-bipyridyl)dichromate(III) Heptahydrate: A Di-*ms*-tartrate-Bridged Binuclear Complex with a Short Intramolecular Hydrogen Bond

Richard B. Ortega, Robert E. Tapscott,*[1] and Charles F. Campana

Binuclear ditartrate-bridged chromium(III) complexes (**1**)

1
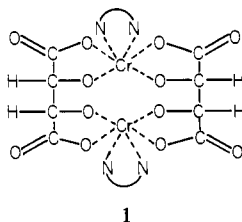
containing 2,2′-bipyridyl (bpy) or 1,10-phenanthroline as the nonbridging ligands have a number of interesting features.[2,3]

Table I. Crystal and Intensity Data Collection Summary

mol formula	$C_{28}H_{35}O_{19}N_4NaCr_2$
fw	858.6
a, Å	12.890 (4)
b, Å	10.364 (3)
c, Å	24.996 (6)
β, deg	90.90 (2)
V, Å^3	3339 (2)
Z	4
space group	$P2_1/c$
ρ(calcd), g cm^{-3}	1.71
cryst dimens, mm	0.6 × 0.6 × 0.6
cryst shape	cubelike with faces {110} and {001}
radiation	Mo Kα (λ = 0.710 69 Å)
abs coeff, μ (Mo Kα), cm^{-1}	7.35
temp, °C	−40 ± 3
scan speed, deg min^{-1}	variable, 2.0–15.0
scan range	0.8° below 2θ (Kα_1) to 1.1° above 2θ (Kα_2)
bkgd counting time	0.5 (scan time)
stds monitored	2 stds every 50 reflcns
2θ limits, deg	2.0–55.0
reflcns collected	$h,k,\pm l$
no. of reflcns collected	7769
unique reflcns	6444
unique data used	4017 with $F_o^2 > 3\sigma(F_o^2)$
$R(F)$	0.064
$R_w(F)$	0.050

They include the first binuclear systems shown to contain bridging *ms*-tartrate ligands (though systems containing bridging *ms*-tartrate derivatives are now known[4]). For many coordination geometries (but not for octahedral), *ms*-tartrate bridging gives an unfavorable ligand conformation.[5] Furthermore, the presence of strong intramolecular hydrogen bonding in these complexes is indicated[2] by an absence of deprotonation for the monoprotic species below pH 11 and by geometrical calculations which predict a close approach between hydroxyl oxygen atoms—a close approach which may be involved in the facile oxidative cleavage of the bridges by permanganate.[6] The *ms*-tartrate bipyridyl derivative also exhibits an unusual solution UV spectrum which has been explained in terms of different $\pi^* \leftarrow \pi$ transition energies for two chemically distinct pyridyl groups of the bipyridyl ligand.[2] Finally, these complexes are known or expected to exhibit large stereoselectivities.[2] Steric considerations[5] indicate stereospecific formation of only one diastereomer (or enantiomeric pair) among the several possible for each isomeric form of the tartrate ligand used. For the racemic-ligand system, the isomers are $\Delta\Delta(RR,RR)$ and $\Lambda\Lambda(SS,SS)$; for the meso-ligand system, β-$\Delta\Delta(RS,RS)$ and β-$\Lambda\Lambda(RS,RS)$.[7]

So that our predictions[2] of a binuclear structure, a close intramolecular approach between hydroxyl oxygen atoms, and stereospecific formation of one diastereomer could be confirmed, as well as for the elucidation of the stereochemical features in hopes of relating these to the unusual UV spectrum and to the ligand oxidation reactions, a crystal structure determination on sodium hydrogen bis(μ-*ms*-tartrato)-bis-

(1) To whom correspondence should be addressed.
(2) Robbins, G. L.; Tapscott, R. E. *Inorg. Chem.* **1976**, *15*, 154. This paper gives incorrect absolute configuration designations for the enantiomers of tartrate. The designations should have been "$d = R,R$, $l = S,S$".
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(7) These designations differ from those used in preceding papers[2,4] which give the isomers as $\Delta\Delta(dd)$, $\Lambda\Lambda(ll)$ and β-$\Delta\Delta(ms\text{-}ms)$, β-$\Lambda\Lambda(ms\text{-}ms)$. The change has been made in order to differentiate by absolute configuration (owing to our recent work with tartrate derivatives[4,8]) rather than by the sign of optical rotation.
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