This formulation shows etolen as a tridentate ligand toward cobalt(III). The inactivity of coordinated etolen in the cobalt(III) complex is thus due to the fact that the complex does not contain a free hydroxy group.

The following etolenH and etolen⁻ complexes[5] were recently synthesized by us: $[Co(etolenH)_2(NO_2)_2]X$ (where X = NO_2^-, NO_3^-, I^-, or $(Co(etholenH)(NO_2)_4]^-)$, $[Co(etolenH)(etolen)]I_2$, $(Co(etolen)_2]I$, $(Ni(etolenH)_2]Br_2$, $[Pd(etolenH)Cl_2]$, $[Pd(etolenH)_2]Cl_2$, and $[Pt(etolen)_2]Cl_2$.

In view of the conflicting data on the cobalt(III) complex, the reactions of etolenH with Co(II) and Co(III) under several conditions of pH, temperature, concentration, catalyst, and solvents were studied critically. It is now apparent that at pH below 8, etolenH behaves as a bidentate ligand coordinated through the two nitrogen atoms. At pH above 8.5, a part or all of etolenH is coordinated as tridentate etolen⁻, coordinated through the oxygen atom as well as the two amino nitrogen atoms. In the case of Co(III), even etolenH may behave as a tridentate ligand. Depending on pH, the metal/ligand ratio, the catalyst, and the temperature of reaction, the following species are apparently capable of existence in the Co(III)–etolenH system.

$$\underset{\text{I}}{[Co(etolenH)_3]^{3+}} \xrightleftharpoons[+\text{etolenH}]{-\text{etolenH}} \underset{\text{II}}{[Co(etolenH)_2]^{3+}} \xrightleftharpoons[+\text{H}]{-\text{H}}$$

$$\underset{\text{III}}{[Co(etolenH)(etolen)]^{2+}} \xrightleftharpoons[+\text{H}]{-\text{H}} \underset{\text{IV}}{[Co(etolen)_2]^{+}}$$

We have not been able to isolate any pure Co(III) compound containing more than 2 moles of etolenH per cobalt atom. All of our attempts to synthesize tris(N-hydroxyethylethylenediamine)cobalt(III) chloride were unsuccessful. Direct oxidation of a solution containing cobalt(II) chloride and etolenH yielded $[Co(en)_3]^{3+}$, $[Co(etolenH)(etolen)]^{2+}$, and $[Co(etolen)_2]^+$ in different proportions, depending on the Co/etolenH ratio and the resulting pH. In some cases, dark red-brown oils, extremely soluble in both water and ethanol, were obtained, but no product of any definite composition could be isolated from such oils by treatment with other solvents, or by precipitation as the tetraphenylborate or the hexanitrocobaltate(III). The reaction of etolenH with $(Co(NH_3)_6]^{3+}$ or with $[Co(NO_2)_6]^{3-}$ was extremely slow at room temperature in the absence of a catalyst. In the presence of activated carbon, the former gave $[Co(etolenH)(etolen)]^{2+}$ or $[Co(etolen)_2]^+$ or a mixture thereof, while the latter gave $[Co(etolenH)(NO_2)_4]^-$, $[Co(etolenH)_2(NO_2)_2]^+$, and some $[Co(etolen)_2]^+$.

The methods of preparation and properties of etolenH complexes other than $[Co(etolen)_2]I$ will be communicated in a separate paper. Keller and Edwards observed the formation of this complex as a purple solution and Tennenhouse first isolated the complex iodide in the solid state. Tennenhouse's method, as modified in the present study, is given below.

N-Hydroxyethylethylenediamine was obtained from Matheson Coleman and Bell and used without further purification. The equivalent weight, as obtained by potentiometric titration, was found to be 52.4 (theoretical 52.1) when freshly opened. *Anal.* Calcd for $C_4H_{12}N_2O$: C, 46.15; H, 11.54; N, 26.92. Found: C, 46.26; H, 11.74; N, 27.12.

Hexaamminecobalt(III) iodide was prepared by the action of potassium iodide solution on a saturated solution of hexaamminecobalt(III) chloride.[6]

Bis(hydroxyethylethylenediamine)cobalt(III) iodide was prepared by mixing 27 g of hexaamminecobalt(III) iodide (0.05 mole) intimately with 2 g of activated carbon (Aqua Neuchar A, West Virginia Pulp and Paper Co.). To this was added 100 ml of a 1 *M* solution of etolenH (0.1 mole) followed by 4 g of sodium hydroxide dissolved in 25 ml of water. This mixture was heated on the steam bath until all of the ammonia was expelled. About 50 ml of water was added and the mixture was heated on the steam bath to dissolve the deep purple product which had formed. The solution was filtered to remove carbon and the filtrate was concentrated to about 30 ml and then cooled in ice. Ethanol was added to precipitate the purple crystals of the complex iodide. These were filtered and washed twice with methanol, and then with absolute ethanol. The product was dried in an oven at 105°, yield 14 g (72%). Larger crystals may be obtained by slowly recrystallizing from 80% methanol. The complex iodide is freely soluble in water, only slightly soluble in methanol, and insoluble (when completely dry) in ethanol, acetone, chloroform, and dimethyl sulfoxide. *Anal.* Calcd for $[Co(C_8H_{22}N_4O_2)]I$: C, 24.49; H, 5.61; N, 14.29; I, 32.40. Found: C, 24.69; H, 5.82; N, 13.96; I, 32.44.

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(5) The formulations given are based on analysis, molar conductance, and visible, uv, ir, and nmr spectra of these compounds. Most of these can exist in more than one stereoisomeric form.

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Infrared Evidence for Single Hydrogen Bridges in Boron Compounds

Sir:

The topic of single hydrogen bridges in certain diborane derivatives has been the subject of several recent communications,[1–3] and some doubt has been expressed whether this structural feature is actually present in the compounds in which it has been suggested. To date, the only physical evidence advanced has been that from nuclear magnetic resonance spectra, the bulk of the arguments being chemical in nature based on stoichiometry and thermodynamics. Although the available evidence strongly favors the existence of single hydrogen bridges, additional supporting results of a physical nature clearly appear desirable.

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Compounds in which the existence of a single hydrogen bridge has been proposed include the adducts $NaBH_4 \cdot BH_3$, $LiH \cdot 2B(CH_3)_3$, and $LiH \cdot 2B(C_2H_5)_3$ whose stoichiometry was established in ether solutions.[4] As part of a broader investigation, we recently have examined the infrared spectra of these adducts in monoglyme or diglyme solutions and believe the results provide supporting evidence for the proposed structure.

It is well known that the presence of a hydrogen bridge in boron compounds is associated with a vibrational frequency in the general region between 1600 and 2100 cm^{-1}, the specific position depending on the molecular environment and symmetry of the motion. Terminal boron–hydrogen bonds on the other hand give rise to bands falling above 2300 cm^{-1}. Although the spectral range for bridge frequencies is rather broad, very few other molecular frequencies fall within it.

In the case of ethers, the spectral region between 1600 and 2600 cm^{-1} is free of infrared bands, and this has enabled us to observe clearly rather broad bands of moderate intensity at 2050, 2100, and 1915 cm^{-1} for solutions of the three adducts, respectively, mentioned above. These bands shift by a factor of approximately 0.7 upon substitution of deuterium for the nonmethyl hydrogen and clearly are due to hydrogen motions. To the extent that bands in this region are characteristic, we believe these data indicate the presence of B–H–B bridges. Although the structure in the case of the $B_2H_7^-$ ion may still be equivocal, the arrangement $[H_3B\text{–}H\text{–}BH_3]^-$ certainly is the most attractive; it is difficult to rationalize any other structure than a single bridging hydrogen in the alkyl compounds.

The diglyme solutions of the adducts were prepared on the vacuum line at temperatures below −20° using procedures described by Brown and Tierney.[4] The solutions were transferred without exposure to air directly into a specially designed infrared cell in which the samples could be maintained at temperatures down to −30°. Under these conditions, the solutions were stable for at least 24 hr and no difficulties were encountered in obtaining spectra. Comparison spectra of the reactants and other boron compounds such as $B_3H_8^-$ were obtained under the same conditions and shown to be different. Details will be published at a later date.

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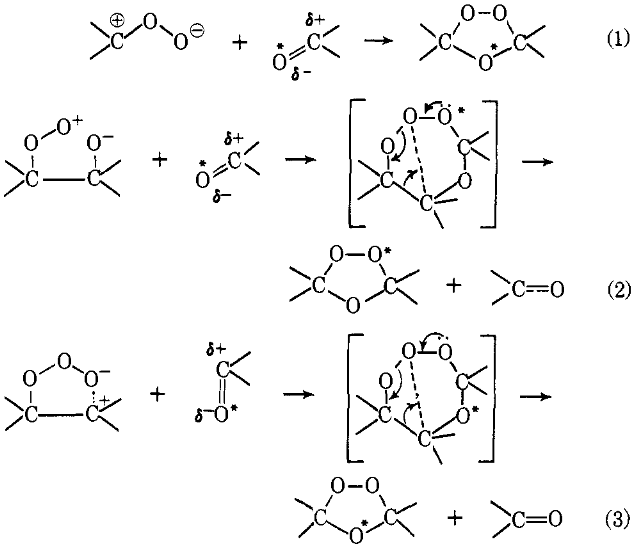
On the Ozonolysis of *cis*- and *trans*-Stilbene in the Presence of Benzaldehyde-^{18}O

Sir:

The object of this preliminary report is to compare, in the case of the *cis*- and *trans*-stilbenes, the mechanisms of ozonolysis proposed by Criegee[1] (1) and by Murray and coworkers[2,3] (2) and to suggest an alternative mechanism (3). The ozonolysis reactions reported below have been carried out in pentane solution in the presence of excess benzaldehyde-^{18}O. The following simplified schemes describe the various mechanistic theories and the corresponding expected labelings ($O^* = {}^{18}O$).



cis-Stilbene solutions (0.1 *M* in pentane) were ozonized in the presence of 0.1 *M* $PhCH^{18}O$ (9.8% ^{18}O) at −78 and 25° with ~70–90% of the theoretical amount of ozone. The ozonides were isolated (after evaporation of most of the solvent) by fractional crystallization and purified by recrystallization in CH_3OH. *trans*-Stilbene was studied in a similar way at −20 and 25°.

From the *cis*- and *trans*-stilbenes ozonized at 25° one obtains an ozonide, mp 74° (lit.[4] mp 74°), which is a 1:1 mixture of the *cis*- and *trans*-ozonides, as shown by the two nmr signals at τ 3.79 and 3.83 (methine protons) and by infrared spectroscopy (bands in CCl_4 at 914 and 952 cm^{-1}). The *cis*-stilbene, ozonized at −78° with excess benzaldehyde, yields (i) the ozonide mixture, mp 74°, and (ii) an ozonide, mp 94° (also observed by Criegee[4]), showing only the nmr signal at τ 3.83 and the infrared band at 914 cm^{-1}. The *trans*-stilbene, ozonized at −20 and 25° in the presence of excess aldehyde, yields two ozonides: (i) the mixture of mp 74° and (ii) an ozonide, mp 82°, which gives only the nmr signal at τ 3.79, but does give the two infrared bands at 914 and 952 cm^{-1}. By comparison with similar systems[3,5] it seems reasonable to assign the *trans*-ozonide configuration to the higher melting compound (τ 3.83) and the *cis* configuration to the compound of mp 82° (τ 3.79).

The mass spectra of the products of mp 74, 82, and 94° are practically identical; two possible fragmentation patterns (a and b) of the ozonide ring yielding *m/e* 122 and 106 are considered, as well as the fragmentation (c) yielding *m/e* 196.

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