Letters to the Editor

The isotope effect of the solvent in the chemiluminescent oxidation of uranium(IV) by the products of the interaction of XeO_3 with H_2O_2 in aqueous sulfuric acid

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We showed previously[1] that the oxidation of uranium(IV) by the products of the reaction between XeO_3 and H_2O_2 in aqueous H_2SO_4 is accompanied by chemiluminescence (CL). This system may be used as a model for investigating photo- or radiolytic reduction of uranium(VI). The time dependence of the CL intensity is expressed by a curve having an induction period, a clearly defined maximum, and further rapid decay (Fig. 1, curve *1*). The characteristic features of the kinetics of the CL observed were explained in terms of a radical chain mechanism involving autocatalysis of the interaction between XeO_3 and H_2O_2 in the presence of uranium(IV), whose reactions with XeO_3 and H_2O_2 serve, in turn, as the source of ·OH radicals, which participate in the chain growth.

We found a kinetic isotope effect, which confirms the participation of hydrogen-containing species in this reaction. As the degree of deuteration of 1 *M* H_2SO_4 increases, the time it takes for the maximum CL intensity to be achieved (t_{max}) increases nearly linearly (see Fig. 1). t_{max} is 7 min in 1 *M* H_2SO_4 and 38 min in a solution containing 86.7 % deuterium. Thus, if we assume that t_{max} characterizes the rate of the overall CL process, the kinetic isotope effect is as high as 5 even at partial (86.7 %) deuteration of the solvent.

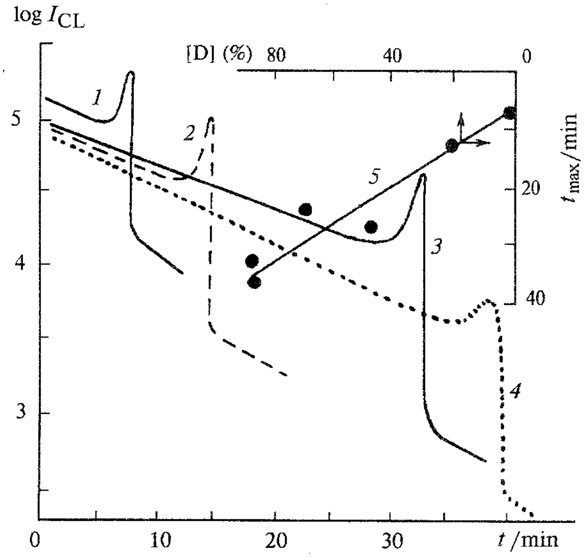

Fig. 1. The kinetics of chemiluminescence accompanying the interaction between U^{IV}, XeO_3, and H_2O_2 in 1*M* H_2SO_4. The content of deuterium in the solution (%): 0 (*1*); 22 (*2*); 46 (*3*); 87 (*4*); the dependence of the time required to achieve the maximum on curves *1—4* on the degree of deuteration of the solution (*5*) (T = 293 K, $[U^{IV}] = 2.5 \cdot 10^{-5}$; $[XeO_3] = 10^{-4}$; $[H_2O_2] = 2.5 \cdot 10^{-4}$ *M*).

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 7, pp. 1341—1342, July, 1994.

This work was carried out with the financial support of the Russian Foundation for Basic Research, project 93-03-12291

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Received February 16, 1994

Chelate synthesis of functionally substituted 2-trichloromethylpyridines

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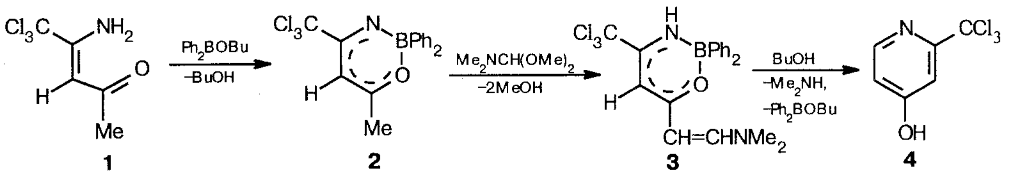
We are proposig new schemes for the synthesis of 2-trichloromethylpyridines *via* chelate-type boron compounds. We found that the diphenylboron chelate (**2**) prepared from 4-amino-5,5,5-trichloro-3-penten-2-one (**1**) reacts with dimethylformamide dimethylacetal to give the condensation product, *viz*, complex (**3**). Boiling the latter in BuOH results in its cyclization to pyridine (**4**) (Scheme 1).

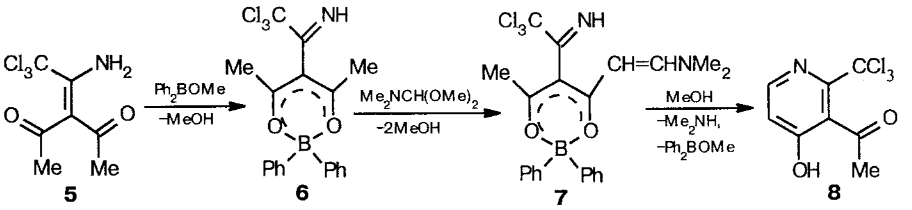
Unexpectedly, it turned out that, when treated with Ph_2BOMe, the *C*-acetyl derivative of enaminone **1**, 4-amino-3-acetyl-5,5,5-trichloro-3-penten-2-one (**5**), behaves as a β-diketone-type chelating ligand, rather than an enaminone-type ligand, and affords complex (**6**), according to the ^1H and ^{13}C NMR spectra. The latter reacts with $Me_2NCH(OMe)_2$ at ~20 °C to yield the condensation product (**7**), which is smoothly converted to pyridine (**8**) when boiled in MeOH (Scheme 2).

The structures of chelates **3**, **6**, and **7** and pyridines **4** and **8** were confirmed by ^1H and ^{13}C NMR and IR spectroscopy and mass spectrometry. The elemental analysis data correspond to the calculated values. The 4-pyridone $\rightleftharpoons$ 4-hydroxypyridine equilibria for compounds **4** and **8** are shifted to hydroxypyridines, which is indicated by the signal at ~110 ppm in the ^{17}O NMR spectrum.

Scheme 1



Scheme 2



Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 7, pp. 1342—1343, July, 1994.