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Selective Oxidation of Methane and Its Homologues to Alcohols Catalyzed by Gold Compounds and a Proposed Reaction Mechanism

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Gold complexes with the bioflavonoid rutin in water catalyze the selective oxidation of methane to methanol by air at room temperature and atmospheric pressure like it occurs in bacteria *Micrococcus luteus* [1]. The present work is aimed at extending the scope of substrates to the nearest methane homologues, ethane and propane, and at studying the mechanism of oxidation of methane and its homologues.

The experimental procedure used in this study was analogous to that in [2], where methane oxidation was catalyzed by the Au(I) complex with rutin. The reagent concentrations were on the same order as in the reaction in [1]. The reaction requires the presence of the reducing agent NADH; therefore, as in [3], gold active toward a hydrocarbon should be in the Au(I) state.

The oxidation of ethane and propane was studied under the same conditions. The reaction products were, respectively, ethanol and 2-propanol. Chromatographic analysis showed the absence of 1-propanol. The yield of the products per mole of Au at 25°C over a period of time of 48 h was 30 mol for methane, 200 mol for ethane, and 220 mol for propane; at 5°C, the yields (72 h) were 15, 40, and 141 mol, respectively. The yield increases in the series of alkanes C_1–C_3. The observed increase in the reactivity along this series is consistent with the decrease in the C–H bond cleavage energy (table).

Ethane and propane are also oxidized without rutin, in the presence of O_2, NADH, $HAuCl_4$, and the Tris–HCl buffer (pH 7.8). The yields of ethanol and 2-propanol in this case decrease to, respectively, 40 and 25 mol per mole of Au (48 h at 25°C).

Figure 1 shows the kinetic curve of propane oxidation to 2-propanol by the Au–rutin complex. The initial acceleration of the reaction is likely associated with the reduction of Au(III) to Au(I). The reaction mechanism can only be suggested at present. In studying this mechanism for methane, we will proceed from the proposed structure of another catalytically active complex, the Au(I) complex with quercetin (**1**) reported by us in [5]. In the first step, the activation of a methane C–H bond (**2** → **3**) occurs upon its oxidative addition to the gold complex. Inasmuch as methylgold complexes are rather resistant to hydrolysis, it should be assumed that the C–O bond formation (**3** → **4**) is caused by the participation of water or oxygen in the process. Gold is not an oxophilic element; therefore, its direct interaction with an oxygen molecule is improbable. If it is assumed that the oxygen molecule in the next step detaches an H atom from the methyl

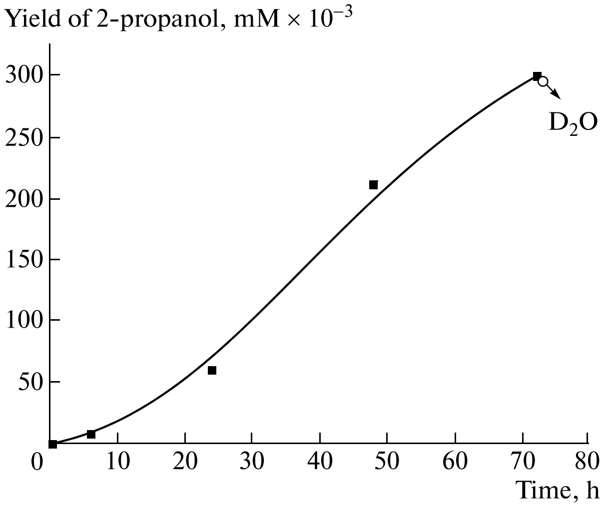

Fig. 1. Kinetic curve of propane oxidation catalyzed by the Au(I)–rutin complex at 25°C.

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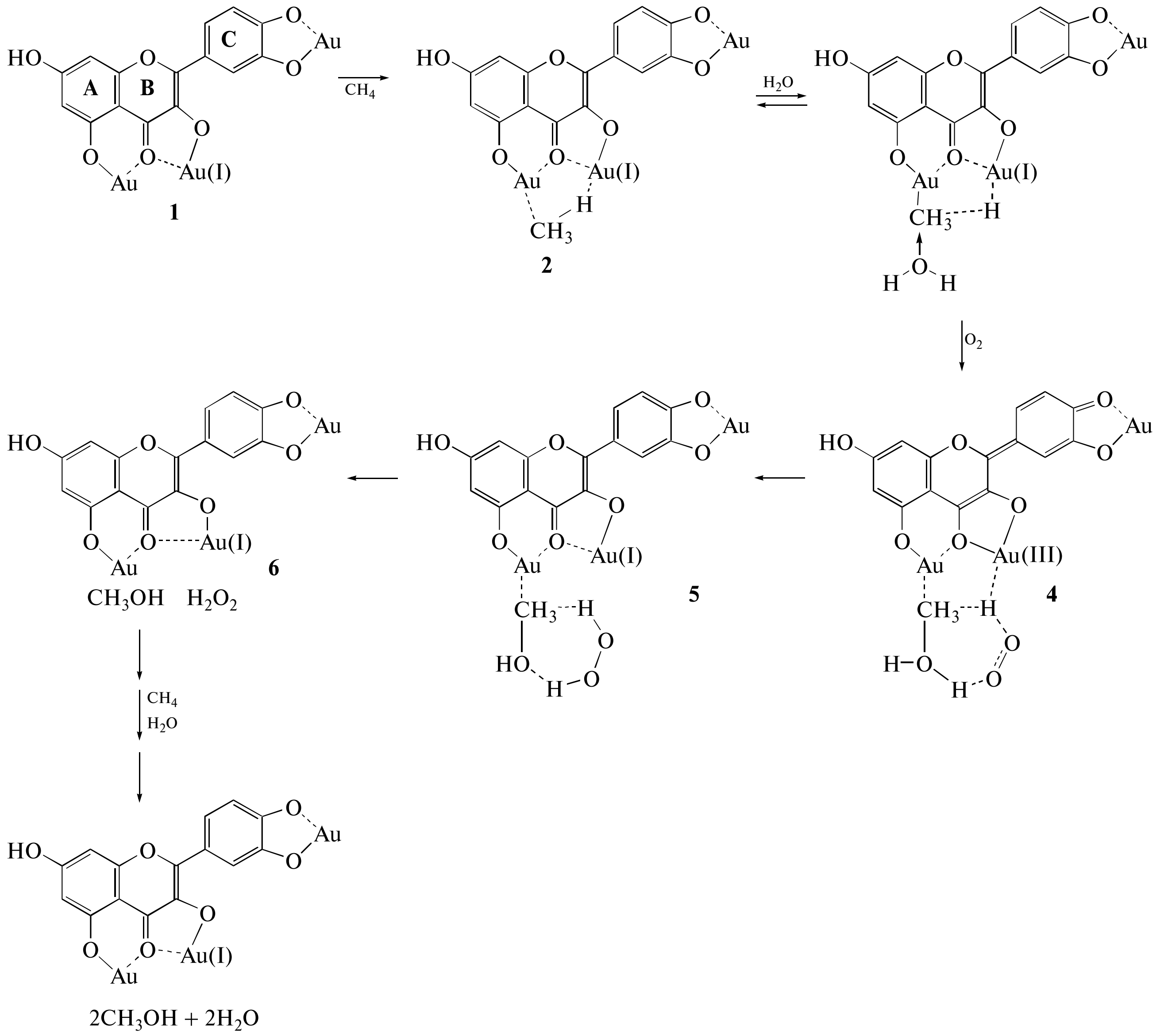
ligand to produce the carbene complex Au–CH_2, the latter could react with water to give CH_3OH. However, in the system where H_2O was replaced by D_2O (99.9%), formation of the isopropyl group in 2-propanol rules out such a possibility (mass spectrometric data). The mass spectra in H_2O and D_2O turned out to be almost identical (Fig. 2). Therefore, we should assume reversible water addition followed by oxygen addition.

The question of why only the Au(I) complexes with rutin and quercetin do catalyze methane oxidation [5] can be clarified by that the remote gold atom (at ring **C**) is in conjugation with two gold atoms (through rings **A** and **B**). This can be explained by the mechanism shown in Scheme 1.



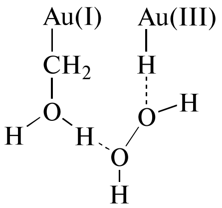
Scheme 1.

Due to the presence of ring C conjugated with rings A and B, intermediate structure 4 should be more stable than in the absence of this ring or conjugation with it.

Stage **4** → **5** of this mechanism yields hydrogen peroxide, which then goes into solution (stage **5** → **6**). From this point on, H_2O_2 acts as the oxidant instead of O_2 (stage **3** → **4**).

C–H bond cleavage energies in methane, ethane, and propane [4]

Alkane	*E*, kcal/mol	Alkane	*E*, kcal/mol
CH_3–H	104.0	$CH_3CH_2CH_2$–H	97.9
C_2H_5–H	98.1	$(CH_3)_2CH$–H	94.5



Methyl group transfer from CH_3ReO_3 to Os_3O_4 followed by formation of CH_3OH was observed in [6].

The oxidative addition of methane to the binuclear moiety of trinuclear Au(I) complex **1** with quercetin was theoretically studied by the PBE density functional method [7] with the use of the extended SBK pseudopotential basis set [8] and the PRIRODA program [9]. The optimized structure of the oxidation product is shown in Fig. 3. The formation of such a structure leads to a decrease in free energy by 28 kcal/mol. The isomeric structure in which the

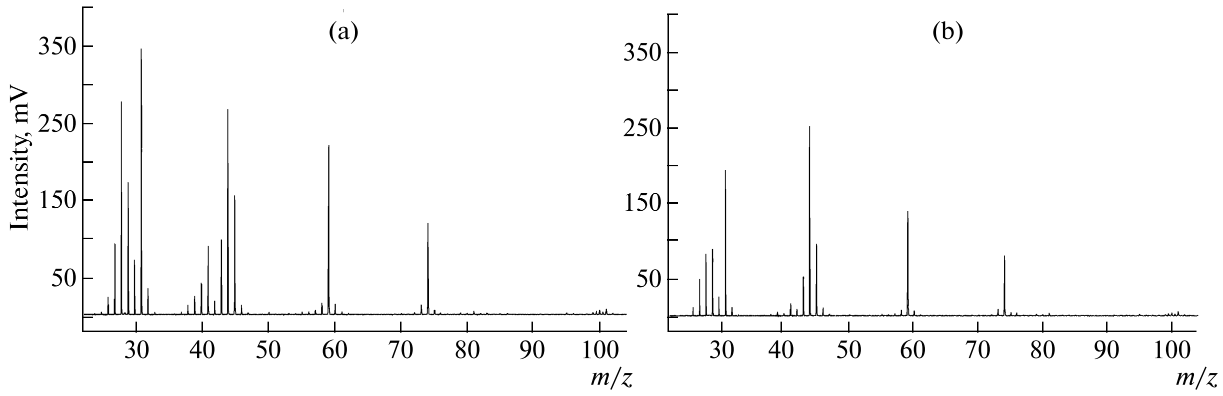


Fig. 2. Mass spectra of gaseous propane oxidation products. Solvents: (a) H_2O and (b) D_2O.

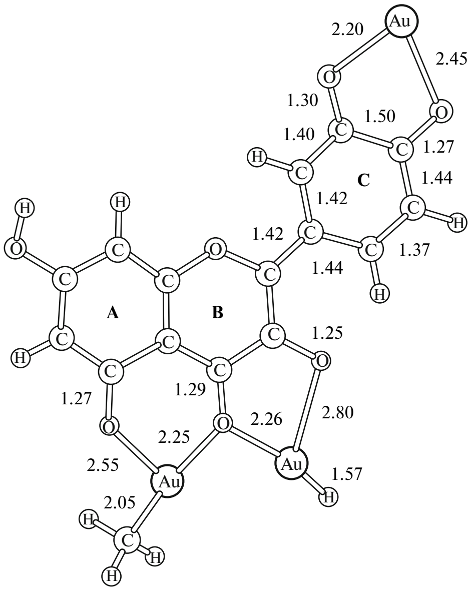


Fig. 3. Calculated structure of the product of methane oxidation catalyzed by the Au(I)–quercetin complex (**2**). Bond lengths are in angstroms.

methyl and hydride ligands change places has almost the same energy. The character of the C–C bond length distribution in the pyrocatechol ring of **1** is evidence of its tendency to rearrange into quinoid form **4**.

Thus, in this work, which is conceptually biomimetic, we succeeded in simplifying the reaction mechanism and explaining the methane activation at room temperature. The same mechanism is proposed for the oxidation of ethane and propane.

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