ISSN 0023-1584, Kinetics and Catalysis, 2009, Vol. 50, No. 4, pp. 583–586. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © I.V. Malakhova, A.A. Shubin, 2009, published in Kinetika i Kataliz, 2009, Vol. 50, No. 4, pp. 605–607.

On the Nature of Radicals Formed in Methanol Catalytic Oxidation

I. V. Malakhova[a] and A. A. Shubin[a, b]

[a] *Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences, Novosibirsk, 630090 Russia*
[b] *Novosibirsk State University, Novosibirsk, 630090 Russia*
e-mail: mira@catalysis.nsk.su; a.a.shubin@catalysis.nsk.su

Received September 1, 2008

Abstract—The quantum-chemical calculations of the hydroxymethyl radical $^{\bullet}CH_2OH$ were performed for the first time and a theoretical EPR spectrum of this radical was constructed. The formation of the hydroxymethyl radical in the reaction of methanol oxidation is thermodynamically favorable. The shape and parameters of the constructed spectrum differed from those for radicals experimentally detected in the catalytic oxidation of methanol using the matrix isolation method. However, they are consistent with the spectrum ascribed to the EPR spectrum of $^{\bullet}CH_2OH$ observed in the direct photolysis of methanol. This result allows one to refine the identification of the nature of radicals formed in the catalytic reaction of methanol oxidation.

DOI: 10.1134/S0023158409040168

As reported previously [1], methoxyl and methyl peroxide radicals are formed in the reaction of methanol oxidation on a mixed-type catalyst (Pt + silica gel) at 450–720°C. These radicals were detected using the matrix isolation method with EPR spectra recording [2]. Analogous spectra of radicals (Fig. 1 shows the typical shape of an experimental spectrum) were observed in a study of the reaction of methanol oxidation on pure silica, as well as alumina and mixed platinum-containing catalysts on these supports (the resulting spectra had the following parameters: $g = 2.030$, $g_\perp = 2.008$, and $A_\perp = 8.7$ G) [3].

In all of our experiments, we failed to detect $OH^{\bullet}$ or $HO_2^{\bullet}$ radicals. This was likely due to the strong adsorption of radicals on the support surface, which was dehydroxylated under pretreatment conditions.

However, the formation of the hydroxymethyl radical $^{\bullet}CH_2OH$ along with the radicals $CH_2O_2^{\bullet}$, $OH^{\bullet}$, and $HO_2^{\bullet}$ has been usually considered in publications on combustion chemistry and atmospheric physics [4–7] because its formation is thermodynamically more favorable than the formation of the methoxyl radical $CH_3O^{\bullet}$:

Reaction	ΔH_r, kcal/mol
$CH_3OH + M = CH_3^{\bullet} + OH^{\bullet}$	92.2
$CH_3OH + M = {}^{\bullet}CH_2OH + H$	98.0
$CH_3OH + M = CH_3O^{\bullet} + H$	104.1
$CH_3OH + M = {}^{\bullet\bullet}CH_2 + H_2O$	91.8.

We performed quantum-chemical calculations for the hydroxymethyl radical and constructed its theoretical EPR spectrum. The equilibrium geometry of the radical in a vacuum (Fig. 2) was calculated using the hybrid electron density functional (UB3LYP with the 6-311g(3df,3pd) basis set) in GAUSSIAN-98 [8]. The

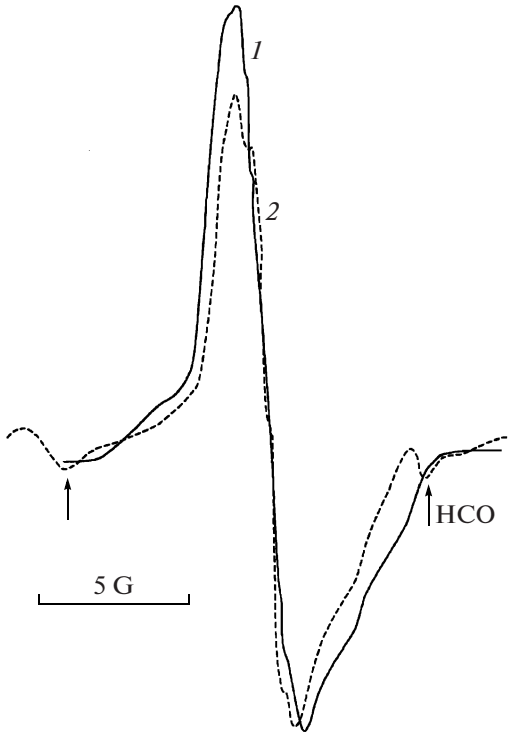

Fig. 1. EPR spectra of matrix isolated radicals (*1*) before and (*2*) after photolysis. $T_{reaction} = 525$°C.

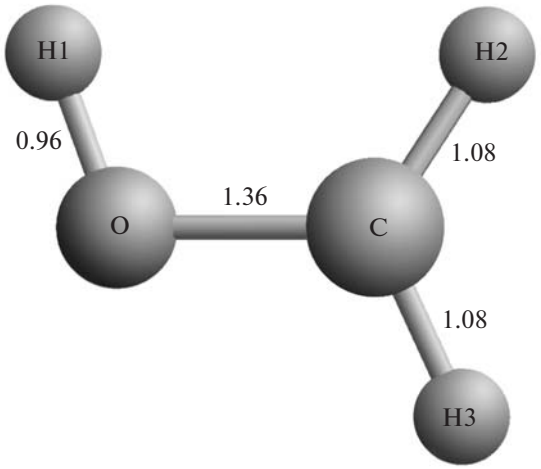

Fig. 2. Geometry of the radical $^{\bullet}CH_2OH$ calculated using the GAUSSIAN program. Bond lengths (Å) are specified.

resulting atomic coordinates were subsequently used to calculate the parameters of the EPR spectrum (*g* tensor and HFI tensors) using the ADF-2005 program [9] (relativistic scalar/spin–orbit ZORA method; QZ4P basis).

The molecular coordinate system was chosen as follows. The *x* axis coincided with the direction of the O–C bond; the *y* axis was directed from H3 to H2; and the *z* axis was the vector product *xy*. The following values were obtained for the main *g*-tensor components and the Euler angles α_G, β_G, and γ_G, which specify the orientation in the molecular coordinate system: $g_1 = 2.0050$, $g_2 = 2.0036$, $g_3 = 2.0021$; $\alpha_G = 312.8°$, $\beta_G = 3.7°$, and $\gamma_G = 342.4°$. The table summarizes the isotropic HFI constants (A_{iso}), the main components of HFI tensors (A_{11}, A_{22}, and A_{33}), and the orientation (α, β, and γ) of HFI tensors with respect to the main axes of the *g* tensor of the radical.

Note that HFI tensors can be calculated not only using the ADF program but also in the GAUSSIAN program. The corresponding control calculation (UB3LYP method; EPR-III basis) gave the orientations of HFI tensors almost identical to those shown in the table. In this case, the main values of HFI tensors differed from those calculated using the ADF program by no more than 10%.

Figure 3 shows the spectrum of the radical $^{\bullet}CH_2OH$ simulated by the ESR1 program [10] with the use of the above parameters for several values of the width (Δ) of an individual line of the EPR signal at a Gaussian line shape:

$$f(x) = \frac{1}{\Delta\sqrt{2\pi}}\exp\left(-\frac{x^2}{2\Delta^2}\right).$$

A comparison between the experimental and calculated spectra indicated that they are different in both the numbers of components and splitting values. At the same time, the theoretically constructed spectrum for width parameters of 2–5 G is consistent with the EPR spectrum of the hydroxymethyl radical shown in Fig. 4. This EPR spectrum was registered by Garibyan et al. [11] in the direct photolysis of methanol frozen at 77 K (where an asymmetric doublet with a splitting of 132 G is ascribed to the formyl radical).

Theoretically calculated HFI constants (MHz) and the orientation of HFI tensors (degree) with respect to the main axes of the *g* tensor for the protons of the radical $^{\bullet}CH_2OH$

Proton	A_{iso}	A_{11}	A_{22}	A_{33}	α	β	γ
H1	–9.7	–24.8	–17.5	13.3	6.0	86.0	83.6
H2	–38.7	–74.3	–35.7	–6.2	305.1	78.3	89.7
H3	–46.9	–82.1	–44.6	–14.0	358.2	99.1	86.8

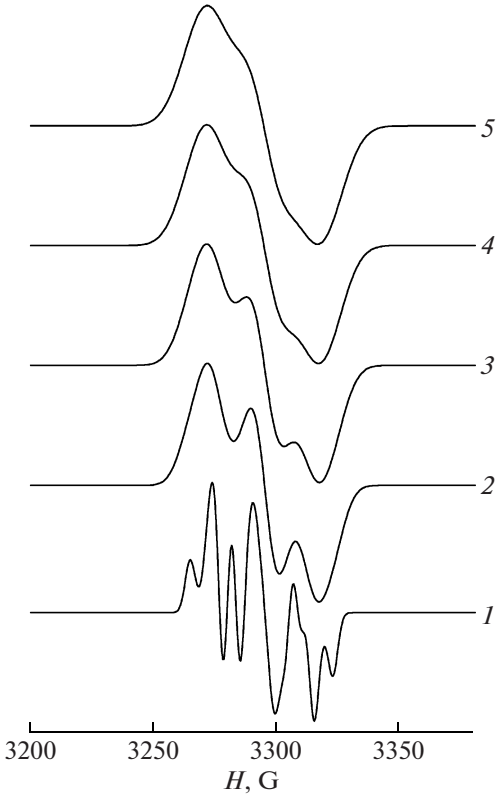

Fig. 3. EPR spectra of the hydroxymethyl radical constructed based on the results of quantum-chemical calculations performed for the following widths (Δ) of individual Gaussian lines: (*1*) 2, (*2*) 5, (*3*) 6, (*4*) 7, and (*5*) 7.5 G.

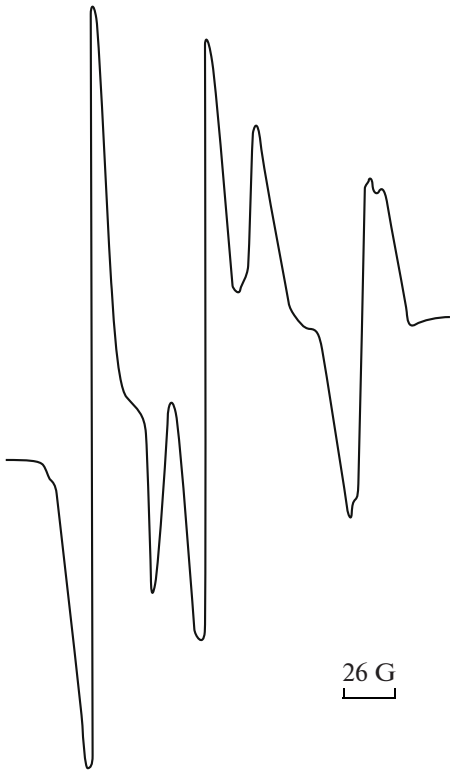

Fig. 4. EPR spectrum of the radicals $^{\bullet}CH_2OH$ and $CHO^{\bullet}$ according to published data [11].

The above consideration allowed us to identify the experimental spectrum obtained by freezing the radicals in the catalytic reaction of methanol oxidation as the superposition of methoxyl and methyl peroxide radicals.

It is likely that, in gas-phase oxidation, the cleavage of the weakest C–H bonds is the primary event. This leads to the formation of $\cdot CH_2OH$ radicals, whereas, under catalytic reaction conditions, the catalyst can affect the activation mechanism of the methanol molecule or cause the isomerization of the primarily formed hydroxymethyl radical into the methoxyl radical. This approach allows us to explain the absence of the thermodynamically preferable hydroxymethyl radical from the experimental spectrum.

REFERENCES

1. Malakhova, I.V. and Ermolaev, V.K., *Mendeleev Commun.*, 1998, vol. 3, p. 83.
2. Panfilov, V.N., *Kinet. Katal.*, 1964, vol. 5, no. 1, p. 60.
3. Malakhova, I.V., Ermolaev, V.K., Danilova, I.G., Paukshtis, E.A., and Zolotarskii, I.A., *Kinet. Katal.*, 2003, vol. 44, no. 4, p. 587 [*Kinet. Catal.* (Engl. Transl.), vol. 44, no. 4, p. 536].
4. Grotheer, H.H. and Just, T., *Combust. Sci. Technol.*, 1993, vol. 91, nos. 1–3, p. 15.
5. Egolfopoulos, F.N., Du, D.X., and Law, C.K., *Combust. Sci. Technol.*, 1992, vol. 83, no. 1, p. 33.
6. Hess, W.P. and Tully, F.P., *J. Phys. Chem.,* 1989, vol. 93, no. 5, p. 1944.
7. Held, T.J. and Dryer, F.L., *Int. J. Chem. Kinet.*, 1998, vol. 30, no. 11, p. 805.
8. *Gaussian 98, Revision A.11*, Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R., Zakrzewski, V.G., Montgomery, J.A., Jr., Stratmann, R.E., Burant, J.C., Dapprich, S., Millam, J.M., Daniels, A.D., Kudin, K.N., Strain, M.C., Farkas, O., Tomasi, J., Barone, V., Cossi, M., Cammi, R., Mennucci, B., Pomelli, C., Adamo, C., Clifford, S., Ochterski, J., Petersson, G.A., Ayala, P.Y., Cui, Q., Morokuma, K., Salvador, P., Dannenberg, J.J., Malick, D.K., Rabuck, A.D., Raghavachari, K., Foresman, J.B., Cioslowski, J., Ortiz, J.V., Baboul, A.G., Stefanov, B.B., Liu, G., Liashenko, A., Piskorz, P., Komaromi, I., Gomperts, R., Martin, R.L., Fox, D.J., Keith, T., Al-Laham, M.A., Peng, C.Y., Nanayakkara, A., Challacombe, M., Gill, P.M.W., Johnson, B., Chen, W., Wong, M.W., Andres, J.L., Gonzalez, C., Head-Gordon, M., Replogle, E.S., and Pople, J.A., Pittsburgh: Gaussian Inc., 2001.
9. Te Velde, G., Bickelhaupt, F.M., Baerends, E.J., Fonseca Guerra, C., van Gisbergen, S.J.A., Snijders, J.G., and Ziegler, T., *J. Comput. Chem.*, 2001, vol. 22, no. 9, p. 931.
10. Shubin, A.A. and Zhidomirov, G.M., *Zh. Strukt. Khim.*, 1989, vol. 30, no. 3, p. 67.
11. Garibyan, T.A., Mantashyan, A.A., Nalbandyan, A.B., and Saakyan, A.S., *Arm. Khim. Zh.*, 1971, vol. 24, no. 1, p. 13.