# Identification of matrix-isolated methoxyl radicals by recording EPR spectra under photolysis

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For the first time gas phase radicals have been observed, using the matrix isolation method, during methanol oxidation on a Pt/SiO$_2$ catalyst. A method of identifying the radicals generated is suggested, which utilises the differing resistance of MeO· and MeO$_2^{\cdot}$ radicals to photolysis using the full light of a high pressure mercury lamp.

It is necessary to identify gas phase radicals and to measure their concentration when studying the mechanisms of gas phase reactions. Spectral analysis is widely used for this purpose. A method suggested by Panfilov[1] and developed by Nalbandyan *et al.*[2] is based on the isolation of the radicals at 77 K in the reaction product matrix, whose EPR spectra are then recorded. The method has already been widely applied in studies of the mechanisms of the gas phase oxidation of various hydrocarbons.[3] Peroxide radical (RO$_2^{\cdot}$) can be easily isolated in the product matrix. Its low chemical activity allows RO$_2^{\cdot}$ transportation from the reaction zone to the zone of product isolation without significant concentration loss.[4] It is, *a priori*, assumed that the EPR spectrum allows identification of the isolated radical.

However, when the reaction produces several types of radicals with similar EPR spectral parameters, for example, when the spectrum is a superposition of the MeO· and MeO$_2^{\cdot}$ spectra, it is difficult to analyse the matrix spectrum. It is well known that these radicals (main intermediates in CH$_4$ and MeOH oxidation) have different reactivities, and initiate different reaction routes. Thus, to understand the reaction mechanism it is important to estimate the relative radical concentrations.

As with radicals HO· and HO$_2^{\cdot}$ the EPR spectra of MeO· and MeO$_2^{\cdot}$ are expected to be similar as regards the axial anisotropy of the $g$-tensor and large value of $\Delta g = g_{\parallel} - g_{\perp}$ and $g_{\mathrm{av}} = 2.014$–$2.015$. Spectral superposition shows the additional broadening of components near $g_{\parallel}$ and $g_{\perp}$, which diminishes the difference between the spectral parameters and thus complicates the estimation of the relative radical concentrations.

In the present paper we suggest a new method of identifying the nature and concentrations of matrix isolated radicals (MeO$_2^{\cdot}$ or MeO·). The method is based on the different behaviour of the radicals under photolysis.

Earlier, based on the results of refs. 7 and 8, we have shown[9] that photoconversion MeO$_2^{\cdot}$ proceeds mainly through reaction (1).

$$\mathrm{MeO_2^{\cdot}} \longrightarrow \mathrm{HCO\cdot} + \text{diamagnetic products} \qquad (1)$$

The concentration of HCO· is *ca.* 1/3 of the initial concentration of MeO$_2^{\cdot}$. The same result was achieved in the photolysis of MeO$_2^{\cdot}$ in an argon matrix.[10] The EPR spectrum of HCO· shows an asymmetric doublet $g_{\mathrm{av}} = 2.001$, the splitting value being *ca.* 130 G. These factors allow ready identification of the HCO· radical, even when spectra from several type of radicals are superimposed.[9]

We have isolated radicals desorbed from the catalyst surface during methanol oxidation by molecular oxygen (pressure 1.33 Pa, methanol–oxygen ratio 1:1 and reaction temperature 820–920 K) when both MeO$_2^{\cdot}$ and MeO· are formed.

The experimental set up is described in detail elsewhere.[11] Absolute methanol, twice de-gassed by crystallization and pumping, passes from the evaporator into the reactor through a capillary. Methanol vapour pressure is regulated by a cooling mixture of CaCl$_2$ and ice. Pre-dried oxygen is accurately metered from a vessel. Catalyst SiP(II), which is a mechanical mixture of silica and platinum black (2 wt%), is pressed in tablets under 50 atm and put over the reactor grid as a one-grain layer. The radicals, together with other reaction products, are frozen out in the side arm of a Dewar vessel installed in the EPR resonator and connected to the flow vacuum system. Radical photolysis in the reaction product matrix occurs under the full light of a 500 W high pressure mercury lamp (DRsh-500, Russia).

Figure 1 presents the EPR spectra of matrix isolated radicals before (*1*) and after (*2*) photolysis. The spectrum shows an asymmetric line typical of paramagnetic species with an axial anisotropy of $g$-tensor, whose $g_{\perp}$ component splits into a quadruplet. Curve *3* in Figure 1 presents a model spectrum simulated using the program of Shubin.[12] The model spectral parameters are equal to the experimental ones: $g_{\parallel} = 2.03$, $g_{\perp} = 2.008$, $A_{\perp} = 8.7$ G. The individual component width 7 G and $A_{\parallel} = 1.02$ G were assumed to be those determined for HO· radicals.[13,14] The Me group was assumed to rotate around the C–O bond. Apparently, the model spectrum is in good agreement with the experimentally obtained spectrum after photolysis. Similar spectra were described,[15] in which radical isolation was used to study methane oxidation on SiO$_2$ and Al$_2$O$_3$ at 900 K, and in methanol oxidation over a catalyst in the total oxidation of hydrocarbons.[9,11]

According to refs. 16 and 17 at a low pressure of reagents at 770–870 K molecular oxygen completely dissociates on platinum, and oxygen atoms react with methanol *via* reaction

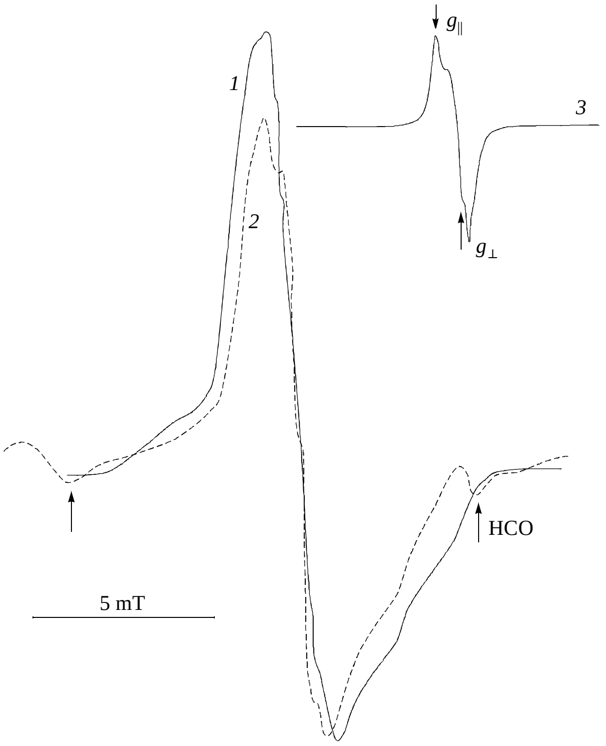

**Figure 1** EPR spectra of matrix isolated radical before (*1*) and after (*2*) photolysis; EPR spectrum (*3*), simulated from the experimental parameters.

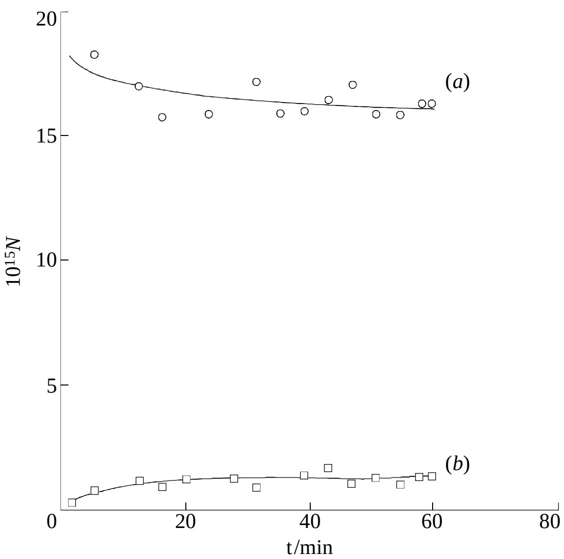

**Figure 2** Matrix isolated radical concentration *versus* photolysis time: (*a*) total EPR absorbance, (*b*) HCO· radical formation.

(2).

$$\mathrm{MeOH} + \mathrm{O}\cdot \longrightarrow \mathrm{MeO}\cdot + \mathrm{HO}\cdot \qquad (2)$$

The maximum reaction rate is attained when the methanol–oxygen ratio in the reaction mixture is 1:1. The reaction route producing methoxyl radicals (2)[17] also produces hydroxyl radicals (HO·) in the same amount, which were recorded by laser fluorescence over platinum, the effective activation energy being 20 kcal $\mathrm{mol}^{-1}$.

In our experiments we failed to record HO· radicals, which is most likely due to either the rapid recombination of HO· on the walls during transportation to the isolation region or strong adsorption of HO· on the $SiO_2$ surface. The effective activation energy for MeO· formation was determined to be 7 kcal $\mathrm{mol}^{-1}$. Such a difference in the activation energies may be explained if we assume that radical desorption limits radical generation. Taking into account the fact that our catalyst is a mechanical mixture of silica and platinum black, we expect that methoxyl radicals form on platinum, as for HO· radicals, and then spill over to the $Pt/SiO_2$ interface, where desorption is easier with respect to energy. This idea is confirmed indirectly by the effect of catalyst training on the rate of radical generation. Thus, 1 h catalyst treatment by oxygen at $T_{\mathrm{tr}}$ = 940 K and $P(O_2)$ = 15 Torr increases the rate of radical generation by 2–2.5 times.

Photolysis produces HCO· radical lines in the EPR spectra. Their contribution to the spectrum intensity is 6%, and the relative intensity of isolated radicals decreases by 20% (see Figure 2). Therefore, we believe that *ca.* 20% of methylperoxide radicals, formed in secondary reaction $\mathrm{MeO}\cdot + \mathrm{O}\cdot \rightarrow \mathrm{MeO}_2^{\cdot}$, convert to HCO· under light exposure, while the photolysis of methoxyl radical does not proceed under our experimental conditions.

Therefore, we may employ the high resistance of MeO· radicals to photolysis, using the full light of a high pressure mercury lamp, as a factor which allows us to distinguish methoxyl and methylperoxide radicals during methanol oxidation using EPR spectroscopy and matrix isolation techniques.

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## References

1 V. N. Panfilov, *Kinet. Katal.*, 1964, **5**, 40 [*Kinet. Catal.* (*Engl. Transl.*), 1964, **5**, 49].
2 A. B. Nalbandyan and A. A. Mashtayan, *Elementarnye protsessy v medlennykh gazofaznykh reaktsiyakh* (*Elemental processes in slow gas phase reactions*), Acad. Sci. Armen. SSR, Erevan, 1975, p. 259 (in Russian).
3 A. B. Nalbandyan and I. A. Vardanyan, *Sovremennoe sostoyanie problemy gazofaznogo okisleniya organicheskikh soedinenii* (*Modern problems in gas phase oxidation of organic compounds*), Acad. Sci. Armen. SSR, Erevan, 1986, p. 227 ( in Russian).
4 E. G. Garibyan, A. A. Muradyan and T. A. Garibyan, *Armen. Khim. Zh.*, 1978, **31**, 466 (in Russian).
5 S. L. Boyd, R. J. Boyd and L. R. C. Barclay, *J. Am. Chem. Soc.*, 1990, **112**, 5724.
6 K. U. Ingold and J. R. Morton, *J. Am. Chem. Soc.*, 1964, **86**, 3400.
7 M. Ya. Melnikov, L. N. Baider and N. V. Fok, *Khim. Vys. Energ.*, 1977, **11**, 338 [*High Energy Chem.* (*Engl. Transl.*), 1977, **11**, 370].
8 S. N. Pak, V. K. Yermolaev and Z. R. Ismagilov, *React. Kinet. Catal. Lett.*, 1986, **32**, 429.
9 V. K. Ermolaev, S. N. Pak, L. G. Krishtopa, Z. R. Ismagilov and K. I. Zamaraev, *Khim. Fiz.*, 1988, **7**, 1141 (in Russian).
10 D. Bhattacharya and J. E. Willard, *J. Phys. Chem.*, 1982, **86**, 962.
11 Z. R. Ismagilov and S. N. Pak, *Catal. Lett.*, 1992, **15**, 353.
12 A. A. Shubin and G. M. Zhidomirov, *Zh. Strukt. Khim.*, 1989, **30** (3), 67 [*J. Struct. Chem.* (*Engl. Transl.*), 1989, **30**, 414].
13 K. J. Kayama, *J. Chem. Phys.*, 1963, **39**, 1507.
14 H. C. Box and E. E. Budzinski, *J. Chem. Phys.*, 1970, **53**, 1059.
15 L. A. Nersesyan, I. A. Vardanyan, E. M. Kegeyan, L. Ya. Margolis and A. B. Nalbandyan, *Dokl. Akad. Nauk SSSR*, 1975, **220**, 605 [*Dokl. Chem.*(*Engl. Transl.*), 1975, **220**, 100].
16 B. A. Sexton, R. D. Rendulic and A. E. Hughes, *Surf. Sci.*, 1982, **121**, 181.
17 M. P. Zum Mallen and L. D. Schmidt, *J. Catal.*, 1996, **161**, 230.

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