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Comment

Comment on “The role of methyl radicals in the reduction of NO by CH_4 over a Ba/MgO catalyst”

[by S. Xie, M.P. Rosynek and J.H. Lunsford]

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The purpose of this letter is to discuss some aspects of experimental data presented in a paper by Lunsford et al. [1]. In a series of publications [1–3], Lunsford et al. used a method they called “variable ionization energy mass spectrometer (VIEMS) system” to explore the reaction of methyl radicals with a solid. The idea of the method is to detect free radicals directly with a mass spectrometer, where gas species are being ionized by electrons with an energy higher than the ionization potential of the radicals but lower than the fragmentation threshold of stable molecules of methane. This method had been successfully applied in a number of publications by other researchers. However, according to our opinion, application of this method to study methyl radicals should be more accurate than it was done in papers [1–3].

Figure 1(A) cited from paper [1] shows a spectrum of a gas mixture obtained at an electron-impact energy of 19 eV. The authors assigned the peak at 15 amu of spectrum (c) to the methyl radicals and the peak at 16 amu to methane. As one can see from that figure, the intensity of the line due to the methyl radicals, $I_{\mathrm{i}}(\mathrm{CH})_3$, exceeds the intensity of the line due to methane, $I_{\mathrm{i}}(\mathrm{CH}_4)$, by a factor of 3.5:

$$I_{\mathrm{i}}(\mathrm{CH})_3 = I_{\mathrm{i}}(\mathrm{CH}_4) \times 3.5. \qquad (1)$$

At the same time, the authors write in the text that the concentration of the methyl radicals, $n(\mathrm{CH}_3)$, is less than the concentration of methane, $n(\mathrm{CH}_4)$, by a factor of 100:

$$n(\mathrm{CH}_3) = n(\mathrm{CH}_4)/100. \qquad (2)$$

Of importance is that the spectrum has been recorded at an electron-impact energy of 19 eV. As is well known, the ion current I_{i} in a mass spectrometer is given by the expression:

$$I_{\mathrm{i}} = kI_{\mathrm{e}}n\sigma, \qquad (3)$$

where I_{e} is the current of the ionizing electrons, k has dimension of length and is a parameter of the experimental setup, which is independent of the sort of species to be ionized, n is concentration of the species in the ionizer of the mass spectrometer and σ is the electron-impact ionization cross-section of the species. Thus the only parameter which is responsible for the dependence of I_{i} on the energy of ionizing electrons and on the sort of species to be ionized, is the parameter σ. Taking this into account, the above cited data would mean that at the energy of 19 eV the ionization cross-section of the methyl radicals exceeds the one for methane by a factor of 350:

$$\sigma(\mathrm{CH}_3)/\sigma(\mathrm{CH}_4) = [I_{\mathrm{i}}(\mathrm{CH}_3)/I_{\mathrm{i}}(\mathrm{CH}_4)][n(\mathrm{CH}_4)/n(\mathrm{CH}_3)] = 350. \qquad (4)$$

The ionization cross-section of methane was thoroughly measured in [4]. The results of this work are summarized in figure 2 (lines 2 and 3). One can see, that both cross-sections depend linearly on the electron energy. At electron energies a few electronvolt above the ionization threshold, such dependence on the energy is quite common for a large variety of substances. The authors of [5] studied the ionization cross-section of methyl radicals in the range from

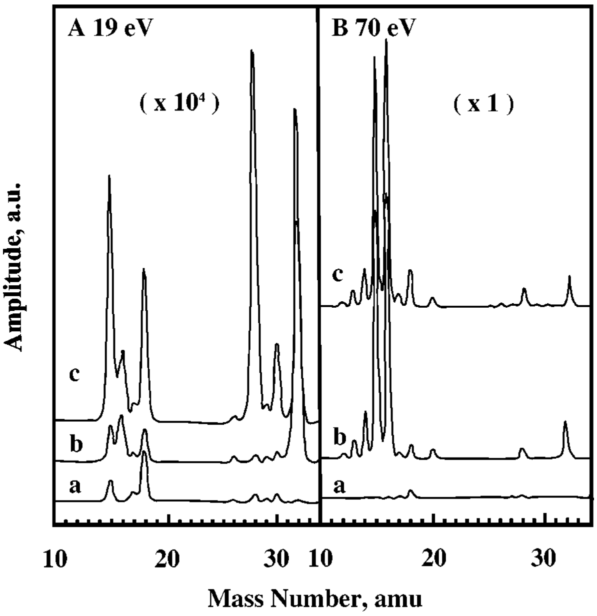

Figure 1. Mass spectra obtained at different electron-impact energies: (a) background; (b) CH_4 and O_2 at 25 °C; (c) after passing CH_4 and O_2 over a catalyst at 775 °C. Cited from [1].

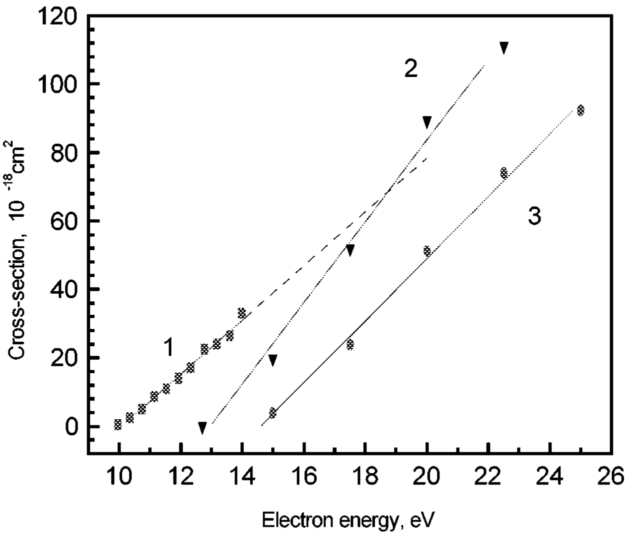

Figure 2. The electron-impact ionization cross-sections of the methyl radicals (line 1, according to [5]) and of molecular methane (line 2). Line 3 – the cross-section of the dissociative ionization of methane to CH_3^+ ion (2 and 3 – both according to [4]).

10 to 22 eV. In this study the methyl radicals were generated by photodissociation of methanol. The results of this work are also represented in figure 2 (line 1). The authors of [5] failed to register methyl radicals at energies above 14 eV due to intensive fragmentation of the initial substance (methanol). This implies the regular dependence of the ionization cross-section of the methyl radicals on the electron energy (dashed line). So, the ratio of ionization cross-sections (4) which can be delivered from the results by Lunsford et al. should be considered as very unusual.

Note also that in their earlier paper [2], Lunsford et al. used ionizing electrons with an energy of 15 eV. They write there that “by using a nominal electron-impact energy of 15 eV, it was possible to selectively ionize only CH_3 radicals” [2]. This contradicts with the well known fact that the methane molecule has an ionization potential of 12.7 eV. Moreover, in paper [3] the same authors have published a spectrum registered at 16 eV showing neither ionization of methane nor mentioning its fragmentation.

We think that the most probable explanation of those discrepancies is an experimental mistake. The authors of [1] either are misleading about the concentration of methyl radicals, or the peak at 15 amu on figure 1(A) is not belonging to the methyl radicals. The reasonable dependence of the peak magnitude on temperature and other reaction conditions, of course, should not be considered as the proof that the assignment of the peak to the methyl radicals is correct.

A simple linear shift of the scale of the electron energies cannot explain the above results as well. The intensity of the fragmentation peak at 15 amu from methane on the spectrum (b) of figure 1(A) reveals that the electron energy is really close to 19 eV. So, spectrum (c) could be explained either by the existence of a certain substance which was not taken into account by the authors of [1] or by the really abnormal dependence of the ionization cross-section of methyl radicals on the energy of ionizing electrons. However, the latter suggestion seems to be very questionable. An unambiguous answer about the ionization cross-section of the methyl radicals can be given only after additional experiments.

Until the discrepancy will be explained we would not recommend a wide use of the numerical data of papers [1–3].

References

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