INVESTIGATION OF A METHANE OXIDATION MECHANISM VIA THE VISUALIZATION OF ELEMENT FLUXES

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Abstract
Reaction pathway analysis is a frequently applied tool in the analysis and reduction of reaction mechanisms. Investigation of element fluxes is a rigorous way of kinetic pathway analysis. Code KINALC has been available for the post-processing of the output files of the CHEMKIN simulation programs. However, plotting the element flux figures provided by KINALC is very human time consuming, therefore a new reaction kinetics visualization tool, called FluxViewer has been developed. FluxViewer presents the species as boxes and the interconnecting reactions as arrows. Location of the boxes and the number of the arrows can be optimized in an interactive way. Development of oxidation processes in reactors and flames can be viewed as a movie. The investigation of the Leeds Methane Oxidation Mechanism via element flux analysis, using KINALC and FluxViewer is presented at plug-flow and premixed flame conditions, at several fuel-to-air ratios. Both KINALC and FluxViewer are freely available from Web address:
http://garfield.chem.elte.hu/Combustion/Combustion.html

Introduction

Detailed knowledge for elementary reactions, advanced computational algorithms and availability of fast computers allow the usage of large, detailed reaction mechanisms for combustion modelling. Such mechanisms for the high temperature oxidation of hydrocarbons typically include dozens or even hundreds of species and thousands of reactions. Several mathematical methods and computation tools are available for the analysis of large complex reaction mechanisms [1], including the reaction pathway analysis.

Reaction pathway analysis and the element fluxes

Reaction pathway analysis is a frequently applied tool for the investigation of complex mechanisms. As an example, Turns [2] discussed the pathway analysis of high temperature methane combustion (see pp. 158-167 and figures 5.4 and 5.5). In the figures of this book, 'each arrow represents an elementary reaction, or set of reactions, with the primary species at the tail and the primary product species at the head'. The width of an arrow is proportional the destruction rate of the reactant [2]. This also means that the widths of the arrows in these figures cannot be compared to each other, since the construction of the reaction network is not based on a conserved property of the species. A suitable conserved property in a complex reaction network is the moles of elements. At any reaction time, the sum of element fluxes considering all species is zero if the stoichiometry of all reaction steps is correct.

The flux of element A from species j to species k through reaction i can be defined [3] as

$$A_{ijk} = \frac{n_{\mathrm{A},j}\, n_{\mathrm{A},k}\, r_i}{N_{\mathrm{A},i}}$$

where $n_{A,j}$ is the number of atom A in species j, $n_{A,k}$ is the number of atom A in species k, $N_{A,i}$ is the sum of the number of atom A in all species on either side of reaction i, and r_i is the rate of reaction step i. Calculation of element fluxes is demonstrated here on the example of reaction step $CH_3 + C_3H_7 \rightarrow C_4H_8 + H_2$. The numbers of H-atoms in the species of this reaction step are 3, 7, 8, and 2, respectively. The sum of the number of H-atoms on both sides is 10. If the rate of this reaction step is r_1, then the fluxes of element H among these four species due to this reaction are as follows:

CH_3	→	C_3H_7	0	
CH_3	→	C_4H_8	$3/10\times8\times r_1 =$	$2.4r_1$
CH_3	→	H_2	$3/10\times2\times r_1 =$	$0.6r_1$
C_3H_7	→	CH_3	0	
C_3H_7	→	C_4H_8	$7/10\times8\times r_1 =$	$5.6r_1$
C_3H_7	→	H_2	$7/10\times2\times r_1 =$	$1.4r_1$

If several reactions are present, the calculated element fluxes should be summed up for all reactions considering all pairs of species. If there are element fluxes between two species in both directions, then not only the separate fluxes are meaningful, but also the difference of these fluxes (called net fluxes). Note, that using the method that was described in the Turns book [2], the calculated reaction fluxes in the example above are all either 0 or r_1.

Software tools for element flux analysis: KINALC and FluxViewer

Program KINALC is a postprocessor to CHEMKIN simulation programs. KINALC works with the CHEMKIN-II [4] and CHEMKIN 3.x [5] simulation packages and making the compatibility with the CHEMKIN 4.x simulation package [6] is in progress. KINALC is a freeware and it is available from the Web [7]. KINALC reads the concentration and sensitivity data from the CHEMKIN 'save' files and carries out 14 different methods for the analysis of reaction mechanisms. These methods span from a simple sorting of sensitivity data to the principal component analysis of the sensitivity matrices, investigation of lifetimes and timescales, and various methods for the derivation of reduced mechanisms. These methods include the calculation of element fluxes. In the case of several elements investigated and many reactions, especially if the element fluxes are calculated at many reaction times, the text output of KINALC is very lengthy and detailed interpretation of it requires considerably human effort.

To facilitate the application of the method of element fluxes, a visual postprocessor code, called FluxViewer, was written. It reads the data file of element fluxes made by KINALC (or by any other code that makes the same format ASCII file) and creates a plot. In this plot the species are represented as labelled boxes and the element fluxes among the species as arrows. If the change of element fluxes is available as a function of time (*e.g.* from SENKIN output) or distance (*e.g.* from PREMIX output), FluxViewer can represent the changes as a movie. In both cases, the change of fluxes can also be inspected as a function of temperature, which is very useful at the study of combustion systems. The width of the arrows is proportional to the logarithm of the element fluxes. Either fluxes or net fluxes of elements can be plotted depending on the interest of the user.

At the visualization of reaction fluxes the key factors are the position of the species boxes and the number of the plotted arrows. At the first usage, FluxViewer places the boxes in a grid. This arrangement can be improved by moving the boxes using the drag'n'drop method to achieve a chemically meaningful final arrangement. Important connections can be emphasized via editing out the less significant arrows by changing a display threshold.

Development and change of the connections among the species with reaction progress can be inspected as an animation. This animation can be paused and the actual picture can be saved for utilization in publications.

FluxViewer is also a freeware and can be downloaded from the Web [8]. As it is a JAVA program, FluxViewer can be used on any platform for which the Java 2 Runtime Environment is available.

Investigation of the Leeds Methane Oxidation Mechanism with element flux analysis

The investigated models were adiabatic, one-dimensional, freely propagating, laminar, premixed methane–air flames and homogeneous, adiabatic methane–air explosions. The calculations were based on the Leeds Methane Oxidation Mechanism [9, 10], which contains 37 species and 175 reversible reactions. The element flux analysis should be carried out with a reaction mechanism that contains irreversible steps only, therefore the original reversible methane oxidation mechanism was converted into irreversible form by program MECHMOD [11]. The simulations were carried out with the CHEMKIN-II package [4]. Program SENKIN [12] was used for the calculations of homogeneous explosions, and program PREMIX [13] for the calculations of one-dimensional laminar flames. Lean (φ = 0.7), stoichiometric (φ = 1.0) and rich (φ = 1.2) mixtures were simulated. The pressure was constant 1 atm in all cases. The initial temperature was 1200 K in the cases of the explosions. The cold boundary temperature of flames was 298.15 K. KINALC 1.9 [7] post-processed the SENKIN and PREMIX save files and generated the input files for FluxViewer.

In Figure 1, the change of the C-fluxes among the species with reaction progress can be seen for a stoichiometric flame. The rate of the reactions become noticeable from about 700 K and at 815 K (see Figure 1a) only few reactions take place, but the C1 path can already be clearly seen. At 1155 K (Figure 1b) the C2 path has been also evolved. Figures 1c and 1d (1500 K and 1805 K, respectively) show that besides the C1 and C2 reaction paths many cross- and side reactions take place. At higher temperatures, the initial reactants have been consumed and at 1925 K (Figure 1f) only the slow $CO \rightarrow CO_2$ conversion can be seen.

Figure 2 presents the comparison of C-fluxes in lean (φ = 0.7) and rich (φ = 1.2) methane air flames. The significant differences are well visible: in the rich flame the C2 path is more emphasized, generation of the CH radical is faster and there are production pathways to C3 species.

Figure 3 shows pairs of pathway plots at the same temperatures for explosions and flames. In the 1400 K zone of the flame reactive small radicals are present due to diffusion; therefore, several inter-conversions are fast. At the same temperature in the explosion the radical concentrations are still low and therefore the most reactions are slow. At 1800 K the rate of reactions in the two systems are similar, but interestingly different reactions are important.

Figures 4a to 4c present the fluxes of elements H, O, and C in a stoichiometric methane-air explosion at 1800 K. These plots complement each other and the comparison of the fluxes of different elements at the same conditions is useful for a good understanding of the properties of the reaction mechanism.

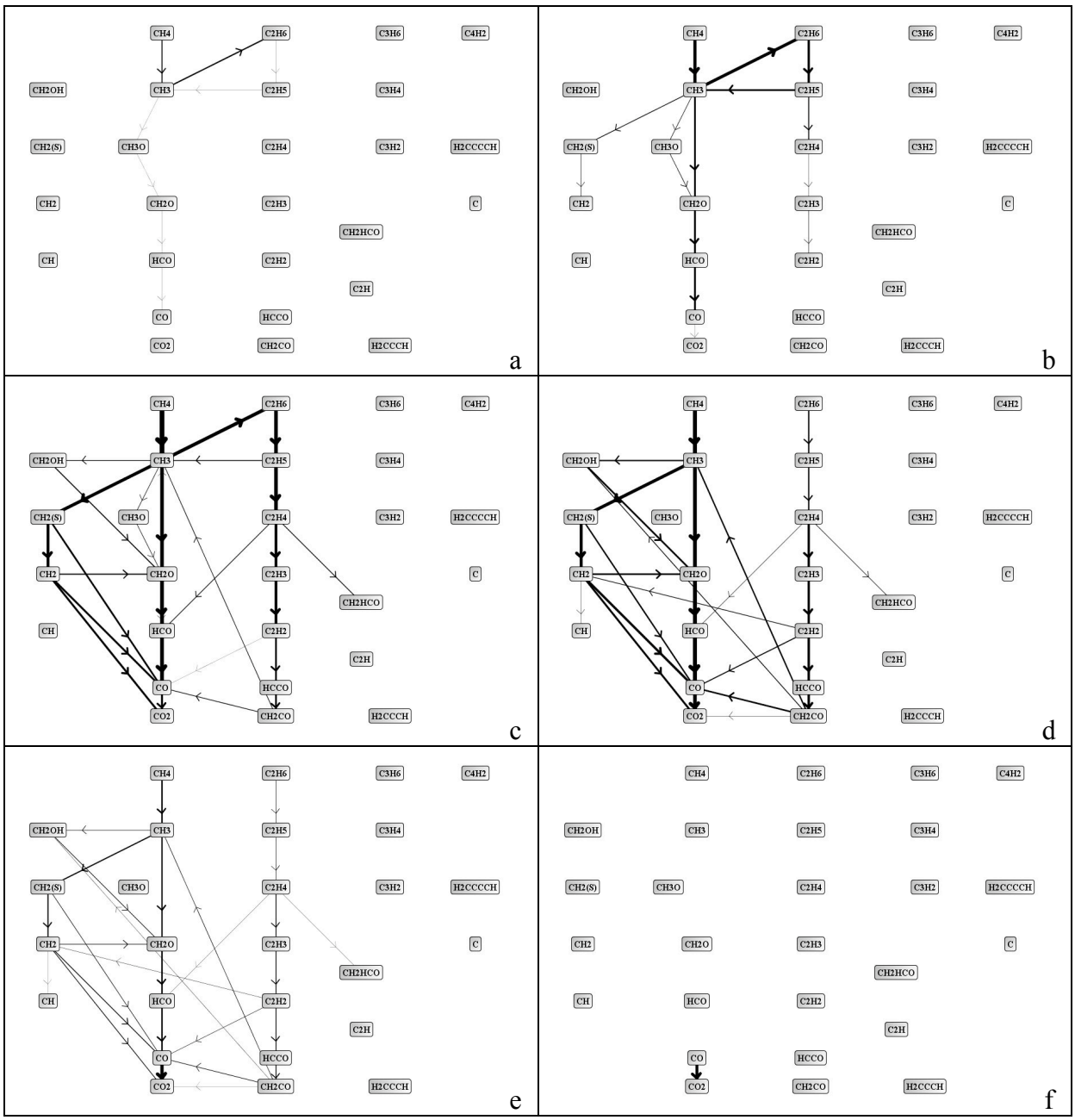

Figure 1. C-fluxes in a stoichiometric methane–air flame. The temperature was 815 K, 1155 K, 1500 K, 1805 K, 1865 K and 1915 K in figures a-f, respectively.

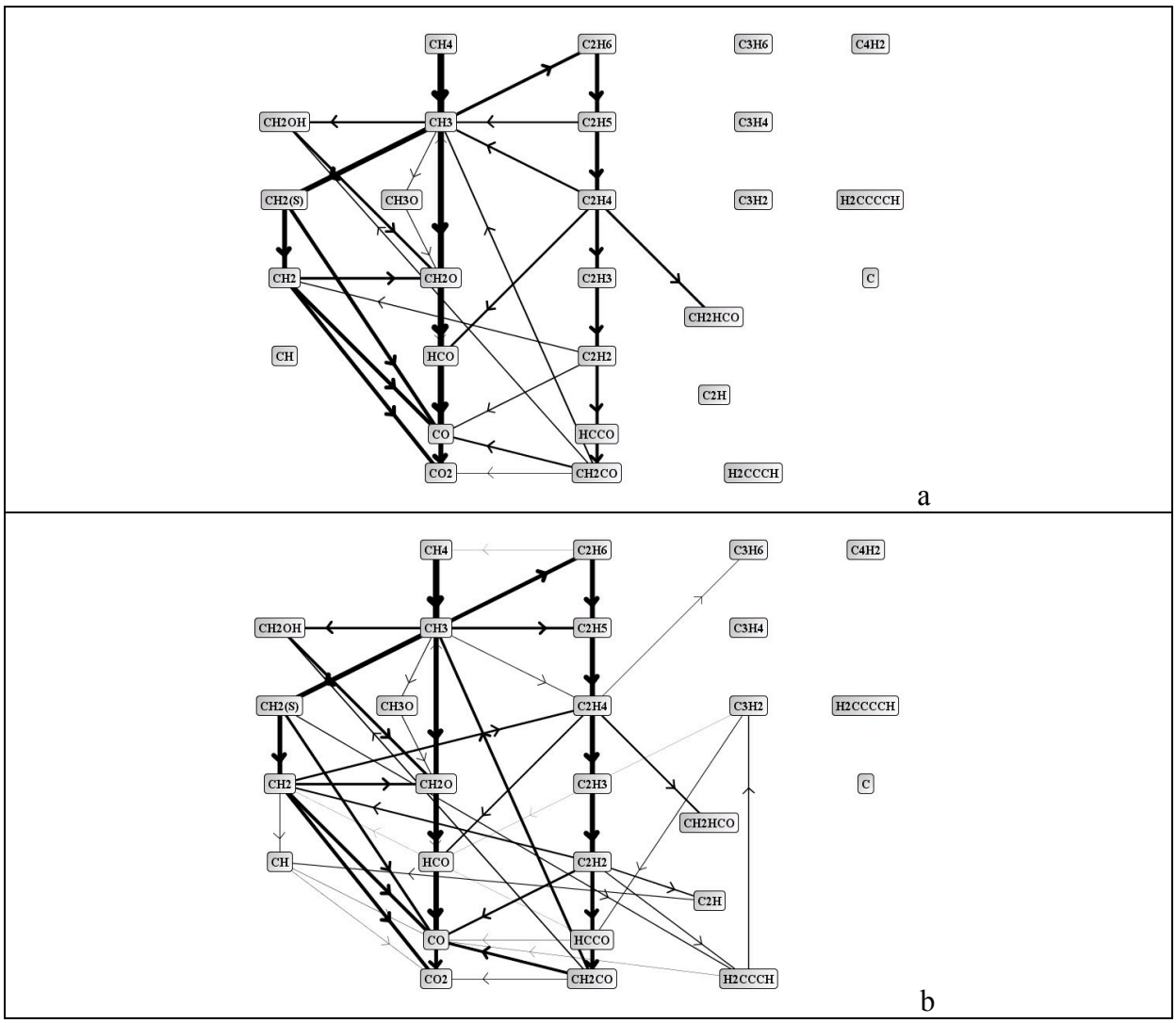

Figure 2. C-fluxes in methane–air stoichiometric explosion in lean (a) and rich (b) mixtures. The temperature was 1455 K (a) and 1755 K (b).

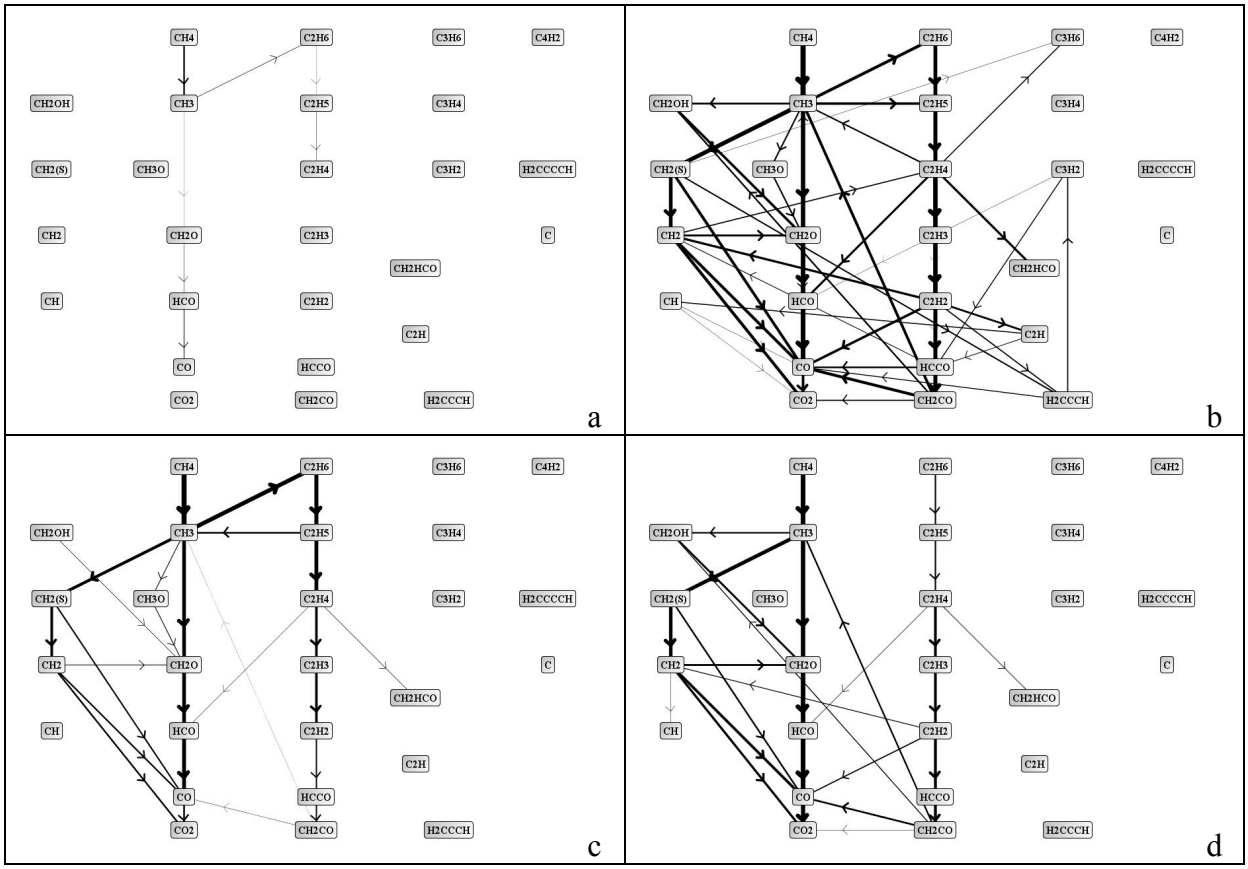

Figure 3. C-fluxes in a methane–air stoichiometric explosion (a and b) and flame (c and d). The temperature was 1400 K (a and c) and 1805 K (b and d).

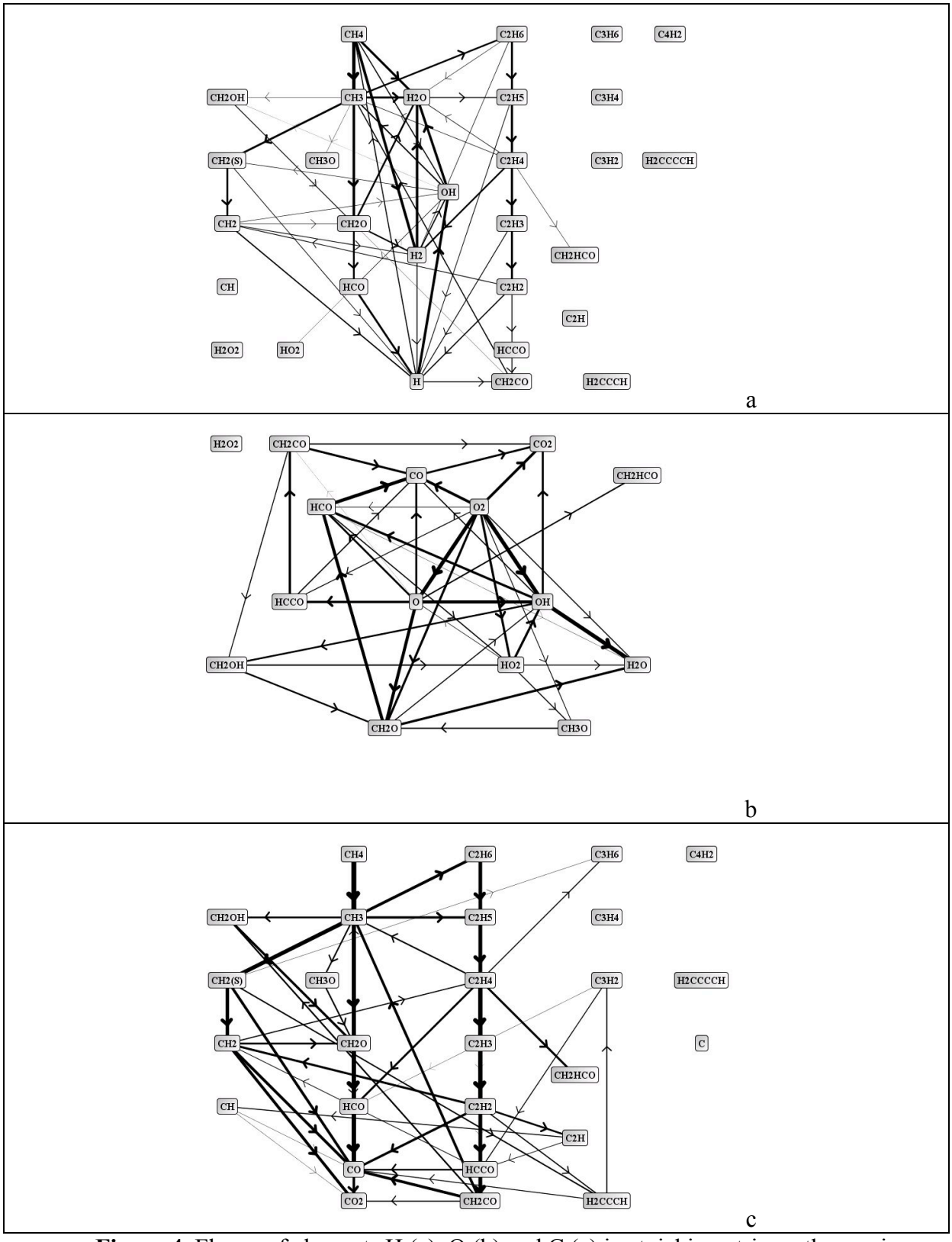

Figure 4. Fluxes of elements H (a), O (b) and C (c) in stoichiometric methane–air explosion at T=1800 K.

Conclusions

Reaction flux analysis provides a useful insight to chemical processes. The concept of element fluxes [3] provides a consistent and well defined way for making reaction fluxes. Code KINALC [7] has been used since 1996 for the analysis of reaction mechanisms utilizing many different methods. These methods included reaction path analysis via the calculation of element fluxes. However, we have found that making plots on the basis of text element flux information is very laborious. For this reason, code FluxViewer was created for versatile drawing of reaction pathways.

FluxViewer is a useful tool for both research and education. At the investigation of a reaction system that is new for the researcher a main problem is distinguishing the 'main stream' species and species that do not connect the reactants and the important products. The movie feature of FluxViewer allows the study of the change of the active parts of the mechanism during the progress of the reaction. Investigation of a well-known system by FluxViewer allows a detailed exploration of the system leading to the understanding of further details. FluxViewer, on the examples of hydrogen and methane explosions and flames has been used in reaction kinetics and combustion courses at the Eötvös University (ELTE). Showing the progress of chemical reactions as flux movies makes a great impression on the students and promotes the reception of these difficult subjects.

In all applications until now, FluxViewer used CHEMKIN data (through KINALC) and was applied for the visualization of high temperature gas kinetics systems. However, any simulation code that makes a FluxViewer format input file can be used as a source of visualization data. This way, FluxViewer can be applied without modification for the study of solution phase or atmospheric chemical kinetic systems.

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