A coherent look at synchronised reactions

Taking his inspiration from the way living cells appear to arrange reactions, **Professor Tofik Murtuza Nagiev** from the National Academy of Sciences of Azerbaijan is shedding new light on coherently synchronised reactions. Using carefully constructed algorithms based on observations of enzymes, Prof Nagiev has developed new models of how reactions may be synchronised on the macroscopic scale.

Professor Nagiev has spent many years researching the complex kinetics of chemical reactions – from his undergraduate days in Chemistry at the Azerbaijan State University, and throughout a long career in the Academy of Sciences. This extensive background places him in the perfect position to consider the next stage in the field, grouping these reactions together to form ensembles which progress quickly and with high selectivity for the final product.

Synchronous parallel reactions, where reactions run at the same time but have no effect on each other, are not uncommon in chemistry and are therefore not of significant interest in the scope of Prof Nagiev's work. More important are conjugated and interference reactions whereby the synchronised reactions affect each other, setting up oscillating conditions which vary product yields.

ILLUSION IN MACROSCOPIC ORGANISATION

Prof Nagiev notes that these effects can also be observed due to physical limitations of a system. Variations in the rate of diffusion of precursors to the active site of the reaction, for example in the Belousov-Zhabotinsky reaction (a classical example of non-equilibrium thermodynamics), give the false appearance of synchronisation. Prof Nagiev identifies this as a distinction between synchronous chemical reactions in the kinetic zone, which are coherent, and in the diffusion zone, which are not.

However, both types of complex reaction are linked by the presence of intermediate compounds which are fundamental to the reaction process. There are both highly reactive intermediates, which are short lived and not included in the final product equations and stable mediators which will appear in stoichiometric calculations (balancing reactants and products according to the laws of conservation of mass).

INTERFERING INTERMEDIATES

The presence of these intermediates evokes the concept of chemical interference, whereby complex chemical reactions are referenced in regard to their phenomena, as opposed to their component characteristics. This paves the way for energetically favourable, highly selective and economical production processes, which harness the synchronous nature of these complex chemical reactions.

Prof Nagiev likens these ensembles of self-organising, self-assembling chemical reactions to the biochemical reactions found in living cells. Here interdependent reactions are brought to close proximity by the activity of enzymes, allowing for reaction rates which would otherwise be impossible to achieve. Mimicking this activity in chemical reactions is the goal of Prof Nagiev's work, such that chemical production processes can be designed to respond to minor changes in composition of the reaction mixture in the same way that biological systems respond rapidly to essentially tiny perturbations.

AN EXEMPLARY REACTION

The only chemical reaction currently being exploited which approaches this situation is the use of hydrogen peroxide (H_2O_2) decomposition to drive the oxidation of substrates in the presence of a biomimetic catalyst. This process is used in production processes such as: methane oxidation to methanol; ethylene oxidation to acetaldehyde and ethanol; propane oxidation to isopropanol; propylene epoxidation and hydroxylation; and ethanol oxidation to acetaldehyde. These have all been

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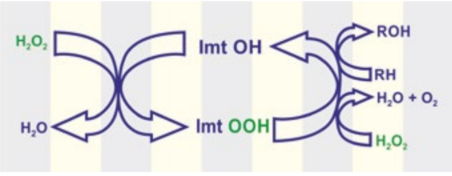
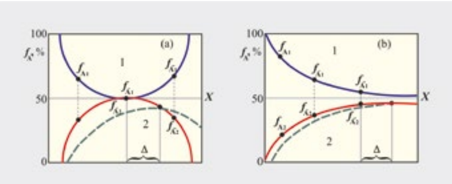
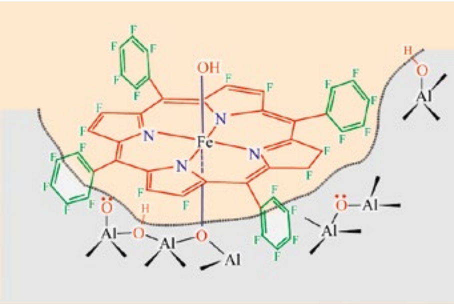


Mechanism of the coherently synchronised catalase and monooxygenase ($RH+H_2O_2=ROH+H_2O$) reactions



Theoretical kinetic curves for interfering reactions (primary 1 and secondary 2) of extreme (a) and asymptotic (b) types; Δ is the phase shift



Catalytic domain design

extensively studied by Prof Nagiev and his team in an effort to elucidate the kinetic similarities which might shed light on further applications of synchronous reactions.

Ethylene oxidation is a particular case in point. Prof Nagiev has shown that, of the two main products ethanol and acetaldehyde, a simple change in reaction vessel temperature is able to significantly skew the production to one product or the other. At low temperatures, the predominant reaction is that of decomposition of H_2O_2 to oxygen, but as temperature increases this yield falls and ethanol takes over as the main product. A further rise then sees this ethanol become an intermediate itself and production of acetaldehyde becomes the predominant reaction. This is an example of chemical interference at work, as the primary reaction drives the secondary, which in turn decelerates the primary.

The synchronisation of propane hydroxylation with H_2O_2 decomposition is a further example of this chemical interference in action. In this case, reaction time is the important

From left: Professor Ahmed H Zewail from California Institute of Technology (Nobel Prize 1999), Professor Tofik M Nagiev from Azerbaijan National Academy of Sciences, Professor Rudolph A Marcus from California Institute of Technology (Nobel Prize 1992) and Professor Maria-Elisabeth Michel-Beyerle from Technical University of Munich, Germany

variable. In the initial stages, production of oxygen through decomposition of H_2O_2 proceeds rapidly to saturation point; it is only once this has produced sufficient oxygen, that hydroxylation can begin to occur. This reaction then proceeds to utilise the oxygen intermediary to oscillating equilibrium, with complete consumption of H_2O_2. The kinetic curves of the catalase (decomposition) and monoxygenase (hydroxylation) reactions clearly show synchronisation and coherence, producing another example of tightly controlled chemical interference.

OPEN HORIZONS

These are just two instances where relatively simple reactions are shown to be coherently synchronised by establishment of their kinetic parameters and interactions. Prof Nagiev believes that this is just the beginning of a rapidly expanding field of chemistry which will harness interfering processes. His work continues to develop algorithms which can assist in investigating and modelling these simple examples. Combining this with an improved understanding of their biochemical counterparts, the enzyme complexes and ensembles which drive cellular activity, will open new opportunities for improving production methods.

According to Prof Nagiev, "Chemistry is on the brink of establishing self-organising and self-assembling chemical systems, [developing algorithms for] a group of chemical reactions to combine in an ensemble to obtain a final product, in a single reaction medium, with high selectivity, in a short time". In pursuit of this goal, Prof Nagiev's team at the National Academy of Sciences continues to probe the current extent of this field, while realising and optimising novel experimental approaches to corroborate their models.

Prof Nagiev focuses on conjugated and interference reactions whereby the synchronised reactions affect each other, setting up oscillating conditions which vary product yields

Q&A

What first attracted you to the study of chemistry?

I was brought up in a family of well-known chemical engineers. My father Murtuza Nagiev was almost fanatically devoted to science, in particular to chemistry. Since my childhood, I have unwittingly participated in the scientific discussions my father held with his colleagues in our house. Growing up my interest in the topics of these discussions was aroused, which subsequently resulted in my professional choice.

What advice do you have for chemistry students today?

Chemistry is so intimately related to the processes occurring in animate and inanimate nature that without its achievements there would be practically no advance in science or in other fields of knowledge, in respect of both fundamental and applied aspects.

I believe that every student who devotes himself to chemistry will be useful in this field. In individual cases chemistry can even lead to fanaticism. I advise the young not to be afraid of new, unconventional ideas, not to be afraid of being misunderstood or even ridiculed. The thing that seemed inconceivable yesterday might become customary tomorrow. This has been repeatedly proven in the history of science.

How does hydrogen peroxide advance our understanding of synchronisation in chemical reactions?

Hydrogen peroxide is a popular oxidant, so called "green oxidant". This substance is widely represented in living organisms, cellular biochemical processes and in general chemistry. The vast majority of biochemical reactions are coordinated – in other words they are coherently synchronised. The same is observed in other areas of chemistry, where these reactions are called conjugate when the result of one reaction causes and accelerates the result of the second reaction. From this perspective, based on the use of hydrogen peroxide in reactions as an oxidant it is possible to develop a model of coherently synchronised reactions, and thereby to study chemical features of these reactions, to develop and evolve the general theory of coherently synchronised reactions. This is the reason I have become interested in this subject and have developed the theory of coherently synchronised reactions from the theory of conjugate processes: conjugate reactions are a particular case of coherently synchronised reactions.

What do you hope the impact of your work will be?

I believe that my work will enable the mechanism of coordinated interaction of biochemical reactions to be revealed. This mechanism might become the basis for the creation of innovative processes in chemical engineering. This will result in a situation where the principles of "green chemistry" (in terms of selectivity) will be reflected in the creation of new applied chemical processes.

What is needed to advance the implementation of coherently synchronised reactions?

Creation of such a design of chemical reactors, which will allow the most effective controlling of the rate of coherently synchronised reactions. This creates the possibility of creating chemical systems, including applied systems, in the most selective way.

On the other hand, examination of biochemical processes in the framework of coherently synchronised reactions will allow mechanisms of their coordinated interactions to be revealed. This will undoubtedly deepen our knowledge of the processes occurring in living systems. As a result of oxygen oxidation, usually at the initial stages, hydrogen peroxide is often produced and its role in coordinated biochemical processes has so far been insufficiently studied. Here one can expect completely unexpected results, which will allow the development of new approaches to the development of innovative technologies.

Detail

RESEARCH OBJECTIVES

Professor Nagiev's work focuses on the macrokinetic theory of coherent-synchronous reactions interaction. Through his work, he has researched areas including the kinetics and mechanism of coherently synchronised reactions, radical chain reactions in the presence of hydrogen peroxide, catalytic reactions of gas-phase oxidation by hydrogen peroxide, oxidative fixation of atmospheric nitrogen, and many more.

BIO

Tofik Murtuza oglu Nagiev is an Azerbaijani scientist, particularly recognised for his work in the fields of chemical kinetics, catalysis and coherently synchronised oxidation by hydrogen peroxide.

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