C. K. Ingold e la geometria del complesso attivato

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RIASSUNTO

Viene presentata una breve riflessione sul perché Sir Christopher K. Ingold [1], uno dei grandi della chimica del XX secolo, largamente ignorato, si sia interessato di spettroscopia molecolare a tal punto da dedicare circa 20 anni alla determinazione della geometria molecolare del benzene (e di alcuni suoi derivati) sia allo stato fondamentale che allo stato eccitato. La risposta che qui viene data è che Ingold fu affascinato dal costatare che il concetto di stato di transizione era stato trasformato da H.Eyring e J.C.Polany [2] in un "complesso attivato", in un vero composto chimico avente una sua entalpia ed entropia di formazione. Sarebbe stato possibile determinare la geometria molecolare del complesso attivato e calcolare la sua energia? Ingold ipotizzò che si potessero usare gli spettri elettronici delle molecole poliatomiche, sperando che uno degli stati elettronicamente eccitati si identificasse con lo stato reazionale. Tuttavia, la geometria del benzene allo stato eccitato si rivelò molto simile a quella dello stato fondamentale. Tutto quel lavoro non risultò utile per lo scopo per il quale era stato concepito. Ingold aveva sperato che il più basso stato elettronicamente eccitato coincidesse con lo stato di transizione, permettendo così di determinare la geometria del complesso attivato, ed aveva ideato una metodologia complessa, ma esemplare, per fare questa misura. Quando fu chiaro che non c'era modo di arrivare alla geometria del complesso attivato per quella via, tutto il progetto perse di importanza. Pochi citano oggi il lavoro sulla geometria molecolare del benzene, che pure è fra i più importanti della spettroscopia molecolare, e nessuno si chiede come mai Ingold gli abbia dedicato tanto tempo. Ingold fu una vittima illustre del mito, tipico degli anni '30-'60, che la fisica teorica fosse ad un passo dal risolvere i problemi della chimica, incluso quello della reattività chimica.

SUMMARY

C. K. Ingold and the activated complex geometry

This article hosts a brief speculation on the largely ignored reasons that brought Sir Christopher K. Ingold, one of the great organic chemists of the XX century, to get involved in molecular spectroscopy and to dedicate about twenty years to the determination of the molecular geometry of benzene, both at the fundamental and excited state. Ingold had been stricken by the theory of H. Eyring e J.C.Polany, which pictured the "activated complex" as a true chemical compound. Would have been possible to determine the molecular geometry of the activated complex of benzene and to calculate its enthalpy and entropy of formation? Ingold hypothesised that one

could use the electronic absorption spectrum of benzene to check if one of the electronic excited states could be identified as the reaction activated complex. However, after many years of work, the geometry of benzene in the lowest excited state resulted very similar to that of the fundamental state, yielding no information on the benzene reaction coordinates. The effort did not pay, was not useful to the original purpose. Ingold had imagined a clever methodology in order to determine the geometry of the electronic exited states, but when it became clear that there was no way to get the right answer by that route, the whole project lost importance. Today very few authors quote the work of Ingold on the molecular geometry of benzene, though being one of the top achievements in early molecular spectrometry. Nobody asks why Ingold has spent so much time on this project. He was a victim of the myth that theoretical physics was going to solve the problems of chemistry, including the one of chemical reactivity.

Key words: UV Electronic Spectra, Activated Complex Theory.

Introduction

Sir Christopher Ingold (1893-1970) [1], one of the great organic chemists of the XX century, was a classical chemist that lived in a traumatic way the transition to quantum chemistry. Despite the many reports and the numerous scholars that wrote on him [2], there is still something to tell, there is a story that deserves some reflection.

I ought to confess that the present effort is not the result of patient historical search on Ingold. Rather, it is my personal viewpoint, based on several years of discontinuous but intense frequentation with C.K. Ingold. When I met him (1959), he was already ahead in age and from long time was a scientist of great fame. The characteristics of this fellow was his extreme availability to help everybody that asked for help. This bothered the many hi-ranked people that worked with him, including his wife that acted as his secretary at the University College. Instead, he continued unperturbed to waste his precious time with the last student.

At that time, I was a student of R.C. Passerini, who originated from the active school of organic chemistry founded by Mangini in Bologna. Passerini had worked for a couple of years with Ingold at the University College in London and, after his call at Catania University, had invited Ingold so often there to succeed to get him interested in our research projects.

Ingold used to come a week per year to Catania and, in his free time, I was in charge to drive him around. We talked continuously chemistry, and he was willing to teach me. Beside his great touch of humanity, he was very cultured and I learned much from him. I do remember everything of our conversations, he insisted on the Ockham razor as the basic criterion on research. I was always astonished for his detailed knowledge of physics and chemistry and, when my admiration was at maximum, he laughed saying that he had much time to learn. Ingold was famous as an innovator in organic chemistry, and at first I was surprised to see how much he was involved in physical chemistry and in particular in spectroscopy.

Since he had the patience to follow my own research project, I went several times to London at the University College to discuss my little piece of work. At the College, faithful to his generous character, he was treating me kindly, introducing me to several spectroscopists and theoretical chemists. He showed me his microdensitometer, just that one used to read the photographic traces of the spectra. He never showed me the organic chemistry labs. He insisted much on the revolution then in act in organic chemistry, which he was seeing as turning from

the empirical discipline of the XIX century into a quantitative and formalised science thanks to the help of physics and of quantum mechanical theory.

One of the merits of Ingold was certainly to have forwarded innovation, favouring the transition from classical to quantum chemistry. However, his enthusiasm for quantum mechanics betrayed him. Initially, I did not catch the contradiction. He had reached the highest success through his work in classical chemistry, he then attempted to go further by means of quantum mechanics, but at the end of his career he realised to have failed his ultimate goal.

When I met him the last time, at the end of 1965, Ingold knew to have been mistaken in 1930 when, fascinated by the quantum mechanical theories on the transition state, he had left the secure path on the mechanism in organic chemistry, to through himself in an uncertain bet.

The Molecular Geometry of Benzene

The textbooks are full of Ingold discoveries. He is perhaps the most important exponent of the English School that at the beginning of XX century contributed to the elaboration of the electronic theory of valence and of the chemical reactivity, defining the inductive and mesomery effects in organic chemistry. Ingold classification of nucleophilic and electrophilic reactions dates about to 1925 [3], when he was studying the Walden inversion [4].

The last reaction was a big mystery of organic chemistry, and constituted a serious anomaly that shined doubts on the chemical theory of that time. Discovered by Walden in 1893 [4], the reaction allows switching, through a simple substitution reaction, from an optically active compound R or S, to his optical antipodes. Despite the Van't Hoff and Le Bell theory had shown that optically activity is bound to tetrahedral carbon, nobody had succeeded to solve this problem and to explain how the Walden inversion occurs.

Ingold hypothesised for this type of reactions a nucleophilic attack to the reaction centre, with subsequent formation of a "transition state" consisting in a "pentabound" planar carbon atom. This hypothesis was then supported by kinetic studies, and a new way to study reaction mechanisms originated since then. He quickly produced a whole systematic of nucleophilic and electrophilic reactions establishing the kinetic methods for the quantitative study of reaction mechanisms in chemistry [1].

In the thirties, he became famous and from his chair at University College dominated the international scene. Organic chemists looked at him a to the innovator that, using the kinetic methods of Arrhenius and Ostwald had succeeded to put organic chemistry on the pathway of quantitative science.

Ingold had further introduced the term "mesomery" in 1925 [1]. His idea was to go beyond the simple concept of tautomery (due to the migration of atoms within a molecule, which causes the existence of two different chemical compounds in dynamic equilibrium).

The concept of mesomery was addressed to explain a different phenomenon: to establish that the fast exchange between simple and double bonds in an unsaturated molecule (for instance, benzene) produces a new chemical species showing intermediate properties. Obviously, it was an empirical concept, based on the classical electronic theory of valence. However, the quantum revolution occurred in these same years, which succeeded to rationalise the chemical bond concept by introducing the internuclear electron exchange, being able to calculate the bond energy. Pauling [5, 6] elaborated the hybridisation theory of the carbon atom orbitals and then the resonance quantum theory between two limit forms.

The success of quantum mechanics gave a solid physical basis to the intuitions of classical chemistry. From that moment it was no more possible to talk of mesomery, the phenomenon had to be described as "resonance". Pauling had succeeded to quantify the phenomenon and to introduce the fruitful concept of "bond order".

These events hit sensibly Ingold; he had to accept a defeat on a discovery of wide meaning. Thus, he concluded that it would be a good idea to study quantum mechanics, and to quit classical chemistry.

Just in those years, the Schroedinger wave function was being applied to describe the chemical reactions and to calculate of the energy of the states involved in the reaction coordinate. The quantum theory of the activated complex was thus formulated (Eyring and Polany [7]). These results prompted the physicists to theorise that it was sufficient to solve the wave function for more and more complex systems, to obtain the exact solution of the behaviour of all chemical reactions. Chemists should only be patient, waiting for the time to develop appropriate calculation methods and to collect sufficient quantitative results.

These theories, and the research perspectives associated to them, obviously resulted in putting in a crisis the classical chemists. Which research project would appear appreciable in view of such new insights? It was no more possible to continue accumulating empirical data based on old schemes!

Ingold had an extraordinary capability of formulating audacious hypotheses to interpret experimental facts. He was inspired by a very fine intuition and by an extremely rigorous analytical work, that he used to reduce the experiments to the essential. He had formulated his theories empirically, without the help of the physical-mathematical tools that now were at basis of the quantum mechanical interpretation of chemistry. He was fascinated by seeing how the transition state concept has been transformed by Eyring in an "activated complex", a true chemical compound having his own enthalpy and entropy of formation.

Would have been possible to determine the molecular geometry of the activated complex and to calculate experimentally its energy? This would be a pioneering project, at page with modern theories! He hypothesised then that one might use the electronic spectra of the polyatomic molecules, hoping that one of the electronically excited states was identical to the reaction state.

Actually, the spectroscopic studies on molecules such as acetylene and formaldehyde had shown that in the excited state these molecules have a different geometry from that in the fundamental state. Acetylene looses his linearity and becomes similar to ethylene, whereas formaldehyde becomes non-planar [1].

However, nothing was then known on the key molecule, benzene, which plays a fundamental role in organic chemistry. If one could identify the molecular geometry of benzene and determine the energy associated to its reactional state, it would become possible to discuss quantitatively the aromatic reactivity problem. This appeared an attractive research project to the Ingold eyes.

Thus, Ingold transformed himself from an organic chemist into a spectroscopist. Starting from 1930 he surrounded himself of theoreticians and spectroscopists that invaded a sizeable portion of the chemistry department at the University College. Of course, Ingold could always count on his excellent coworker E.D. Hughes, who was supervising the students in the organic chemistry lab and was keeping on the original project on the mechanisms of nucleophilic and electrophilic reactions.

Nobody at that time noticed the drastic change which had occurred in the research interests of Ingold, and also later his biographers appear to largely ignore it. This might happen because Ingold was able to direct his old research project through his many students, and because Hughes was so faithful never to dissociate himself from collaborating with the master. However, when Ingold died, lined up on the shelves behind his desk, lied at least 50 meters of PhD theses that remained unpublished. A waste of talent and precious information, a big price that Ingold paid to his decision to develop the new project.

He studied spectroscopy, working to the infrared spectrum of benzene in order to extract from it the molecular geometry of this compound at the ground state. It was a frantic job; nobody had deduced the molecular geometry of a polyatomic molecule containing 12 atoms.

He had to resort to the isotopic substitutions with deuterium in order to distinguish the combination bands and the harmonic of various order, and to obtain information on the force constants necessary to the calculate the molecular geometry of benzene. Huge distillation columns for the distillation of heavy water were built in the basement of the College, reaching the ceiling of the top roof. A score of new specialists (David Craig, Thomas Dunn, Edward Teller, among others) worked together with the chemists. Also Kohlrausch, the famous infrared and Raman expert of Wien, came in tight relation with Ingold.

Finally in 1936, a series of very detailed articles appeared, describing the molecular geometry in the fundamental state [1]. This result was important in itself, none technique had till then produced precise structural information on benzene in the vapour state.

Ingold had spent his energy in this adventure and had shown of what he was capable, but his effort was only half way. He knew the molecular geometry at the fundamental state, but he had now to attack the problem of decoding the vibrational fine structure of the electronic spectra and, making the difference with that of the fundamental state, be able to deduce the geometry of the electronically excited states.

As predictable, the new target took 10 years, and in 1946 another series of articles [1] appeared, describing the geometry of benzene in the first excited state, the one of lower energy.

It had been a huge effort for Ingold, who was not a spectroscopist. It absorbed all his intellectual energy, distracting him from his initial work as an organic chemist and from the study of the chemical reactions mechanisms. As the giant that he was, he continued to follow those studies but did not show any more the creativity that distinguished him in the past. He had expected much from the spectroscopic work. Unfortunately, however, the geometry of benzene at the excited state showed to be very similar to that of the ground state. All the effort showed to be useless for the purpose for which it had been conceived.

Ingold hoped that the lowest excited state was identical to the transition state, thus allowing determining the geometry of the activated complex, and had conceived an exemplar methodology to make this measurement.

When it appeared that there was no way to determine the geometry of the activated complex by following that route, the entire project lost importance.

Few quote today the work on the geometry of benzene, which is however among the most important results in molecular spectroscopy, and nobody is puzzled at the reason why Ingold spent so much time on it.

Ingold was a victim of the myth that quantum mechanics was a short step from solving the problems of chemistry, including chemical reactivity. However, the prize at stake was worth the game, and Ingold was still willing to smile when he told me this story.

Appendix

I do remember that Ingold was present in the lab on a day (1961) when I was trying to record the electronic spectrum in vapour phase of an aromatic compound showing a relatively poor volatility: thiophenol. Since the intensity of the trace recorded was very low, I had used the gas cell with the longest pathway available in the lab, but still it was not sufficient to detect the weak absorption caused by the fine structure of the vibrational band of thiophenol at about 300nm (the transition is weak because it is electronically forbidden).

I was embarrassed for the presence of Ingold, but luckily succeeded in increasing the temperature of the cell. The vapor tension of thiophenol raised enough to make the spectrum more intense, and the vibrational peaks become detectable.

However, those spectral peaks, unequivocally belonging to a vibrational fine structure of an electronic transition of B_{2u} type, characteristic of benzene and its derivatives, should not appear there. The vibrational band observed was expected to correspond to a transition of type B_{1u}, not to a B_{2u} transition.

This unsupported expectation followed from a theory about the expansion of the valence shell of sulfur that, according to Passerini, might be operating in sulfur aromatic compounds such as thiophenol, thioanisole, diphenylsulfide. This fascinating hypothesis (actually made by Ingold during private talks) implied that, different from the analogous oxygen compounds, in the sulfur compounds was operating a resonant system where one of the limit structures had the sulfur atom and the aromatic ring linked by a double bond, thanks to the involvement of the 3d orbitals of sulfur [8].

The experimental evidence for that hypothesis lied just in the electronic spectra of some aromatic sulfur compounds, since they show a red shift with respect to the corresponding oxygen compounds and also increased absorption intensity. This had been interpreted by Ingold (as he told me at that time) as evidence for the disappearance of the benzene electronic transition of B_{2u} type, which is unperturbed by resonance forms, and for the appearance of a new and stronger transition of B_{1u} type, perturbed by the conjugative effect between sulfur and benzene ring.

Unfortunately, previous researchers had recorded the spectra in solution, where the vibrational fine structure is lost because of the interaction with the solvent. On the contrary, my measurements in vapor phase allowed detecting the vibrational fine structure of the unperturbed benzene transition, excluding any resonance form involving a conjugation with sulfur. Ingold made me to repeat several times the measurements, using also thioanisole, and to calculate as exactly as I could the wave numbers of the benzenoid vibrational transition (980 cm^{-1}), but at the end he was convinced.

He pointed out to Passerini the importance of these findings, offering to publish a note where he would take on himself the responsibility of the wrong interpretation of the spectra (since his name did not appear on the original paper), but everything ended up in a drawer.

Later, with the help of Ingold, I was able to convince Passerini to publish only a short note reporting the thioanisole electronic spectrum in vapor phase on the local academy bulletin [8], and the work lies there since then.

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