The Discovery of Chemically Induced Dynamic Polarization (CIDNP)

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If spectrometers seem to 'misbehave', this can be very annoying to the operator and cause him a lot of trouble. It may, however, mark the start of a new episode in Science and initiate a hunt for the explanation of a surprising observation, – possibly even of a new phenomenon, – which in physics may subsequently be called an 'effect'.

Such was the case in the summer of 1965, when I had started out as a graduate student at the Technical University of Darmstadt, Germany, under the supervision of my advisor, Professor *Karl-Heinz Hellwege* (1910–1999), head of two institutes, namely the Institute of Technical Physics and of the 'Deutsches Kunststoff-Institut' (German Plastics Research Institute) (*Fig. 1*).

Fig. 1. *Deutsches Kunststoff-Institut* (German Plastics Research Institute), *established in 1951*

Professor *Hellwege*, like many others of his contemporaries in Science in Germany, had started his education in physics prior to World War II and had received his Ph.D. in 1934 at the University of Göttingen (Germany) where he subsequently completed his 'Habilitation' in 1938 as well. After a long *interim* due to World War II, he continued with his research there, *i.e.*, at a period in time, where it was extremely difficult to conduct any scientific experiments, because of a lack of virtually all prerequisites. Among the latter, liquid helium as a coolant represented an especially scarce commodity, and typically it was not available at all. In this desperate situation, liquid hydrogen had to serve as a substitute, no matter how dangerous. Accordingly, an accident occurred that took some fingers away from one of my advisor's hands. This, and some other 'hang-ups' brought it about that my advisor was very skeptical of chemistry in particular, even though within the German Plastics Research Institute that he headed from 1955 to 1968, there was a rather sizeable department devoted to polymer chemistry.

In his two institutes, Professor *Hellwege* had established an infrastructure of various research groups, the leaders of which he used to refer to as 'Landesfürsten'. This German expression stemmed from the dominance of German politics and the western part of Germany along the Rhine river by the French Emperor *Napoleon* after the French Revolution, and it refers to *Napoleon*'s assignees of power who ruled over individual provinces. Essentially, therefore, a genuine 'Landesfürst' originally used to be a sort of duke, but in Professor *Hellwege*'s 'empire' it implied that he was a sort of '*Napoleon*'. He made that known beyond the shade of a doubt in greeting his subordinates (including myself) with 'good morning', when he noticed them working prior to 8 a.m., but should someone come a bit later, he was greeted merely with 'good day'. In addition, he used to lecture on Saturdays, and he threatened not to return or correct a graduate student's thesis any sooner than after a period of three months, should they dare not to attend his (admittedly interesting) Saturday lectures.

Being aware of these 'high standards', I joined the Polymer Physics Department of his German Plastics Research Institute nevertheless, and I was assigned to the group of Dr. *Uwe Johnsen*, whose research comprised various analytical techniques, especially different kinds of spectroscopy. Dr. *Johnsen* had served in World War II, and as a consequence he had suffered a head injury that caused him severe headaches, sometimes for extended periods of time.

One particular project within Dr. *Johnsen*'s group devoted to conduct research using electron paramagnetic resonance (EPR), – also called electron spin resonance (ESR), – was carried out by a senior postdoctoral fellow, Dr. *Hanns Fischer*. Him I knew even before joining the German Plastics Research Institute, because both of us had joined a student fraternity, called '*Hasso-Borussia*' at Darmstadt. Being a rookie there, called 'fux' (with a faint relationship to the animal called fox) in the typically and traditional nomenclature of such fraternities, I was assigned to the assembly of such rookies just like me, a party of about twenty other 'füxe', called the 'fuxenstall'. Again traditionally, such a 'fuxenstall' has a leader, called the 'fuxmajor'. At 'official' occasions, the members of *Hasso-Borussia* wore a colorful uniform (and still do nowadays), whereby the colors consist of orange and black components. Every member of this and similar fraternities wears a one inch-wide ribbon, in the case of *Hasso-Borussia* in the colors black-white-orange, strapped diagonally across the chest. The ribbon of the 'füxe' is simply orange – white – orange. The 'fuxmajor' in particular differs from the rest and other officers of the fraternity in so far as he wears both the black-white-orange ribbon and that of the füxe in crossed form of two opposing diagonals across his chest. Furthermore, he wears a genuine foxtail strung around a hat or cap, which in case of *Hasso-Borussia* is orange and decorated with a specific emblem, a kind of identifier or trademark for any individual fraternity (*Fig. 2*).

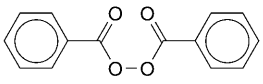
It was in this capacity of 'fuxmajor' that I first got to know *Hanns Fischer*, who – being about 4 years older than I, had joined the *Hasso-Borussia* fraternity a few years earlier, and consequently he had a more senior status accordingly. My experience during this time from 1959 through 1960 must not have been too bad, because it was due to this relationship that I had decided to join the same department of the German Plastics Research Institute in 1962, in which he had previously obtained his masters degree and subsequently his doctorate in physics. At the time of my joining, *Hanns* was not quite a group leader yet. This did occur, however, shortly thereafter, but it required

Fig. 2. *Student fraternity* Hasso-Borussia *at the Technical University of Darmstadt*

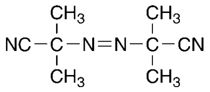
his 'Habilitation', a sort of second Ph.D. thesis on a topic different from that of the first one and an associated second oral exam, which was then still an essential prerequisite in Germany for candidates interested in a university career.

Having taken that hurdle successfully, *Hanns Fischer* was appointed leader of the group Electron Spin Resonance (ESR), initially a body of 3 people. *Hanns*' group was split off from Dr. *Johnsen*'s group, who retained IR and NMR spectroscopy under his own supervision. Being a member of the latter, I was supposed to determine the stereochemistry of poly(vinyl chloride) (PVC) and other vinyl polymers as the topic of my thesis for obtaining a diploma in physics (equivalent to a M.Sc. degree). Actually, after the pioneering work of *Ziegler* and *Natta* with respect to stereochemical polymerization (*Nobel* Prize in 1963), it had become important to identify a physical method that would allow determining the exact degree of stereoregularity of such polymers. Initially, this was done using IR spectroscopy, but Dr. *Johnsen* had the hunch that it should also be possible using NMR spectroscopy instead. Unfortunately for him, just prior to my joining *Johnsen*'s group, the race to demonstrate this claim first had already been lost to *F. A. Bovey* of the Bell Telephone Research Laboratory at Murray Hill, New Jersey, USA [1]. Disappointed about this lost chance, I was supposed to attack other vinyl polymers accordingly. Furthermore, I was in charge of maintaining the NMR spectrometer, a *Varian DP 60*, consisting of a high voltage electromagnet (operating at 2000 volts!) equipped with a stabilizer based on a most sensitive mirror galvanometer (sitting on top of the electromagnet shown in *Fig. 8*), which hated power failures and thunderstorms, when the voltage would fluctuate beyond its tolerance. In this case, the mirror would rip off, and it was my task to fix the dilemma, a most frustrating exercise of patience and skill.

Furthermore, it was my task to apply NMR spectroscopy in a service mode to any challenging research product as they typically occurred in the Department of Chemistry, headed by Prof. *Dietrich Braun*. An Egyptian graduate student of this Department, *Ibrahim Aziz El-Sayed*, who later became a research chemist at the German *Bayer* Company at Leverkusen, had been assigned by Prof. *Brown* to figure out the structure of a mysterious product he obtained when polymerizing maleic anhydride using a variety of polymerization catalysts. According to the knowledge of those days, maleic anhydride 'did not homopolymerize', rather it was well known and used industrially to copolymerize with a variety of other co-monomers like styrene or acrylonitrile. *Ibrahim* had found, however, that maleic anhydride did indeed homopolymerize, albeit under loss of carbon dioxide to something mysterious that could not properly be described with a label like 'poly(maleic anhydride)' as far as its likely structure was concerned. The matter was even worse in so far, as *Ibrahim* obtained very different polymeric products depending on the polymerization catalyst he used. When using typical free radical initiators like either azobisisobutyronitrile (AIBN) or dibenzoyl peroxide (BPO), he obtained a very different type of polymer as opposed to using pyridine, for example, for which he assumed an ionic pathway of polymerization for the maleic anhydride.



Dibenzoylperoxide (BPO)



$$\mathrm{NC-\overset{CH_3}{\underset{CH_3}{C}}-N{=}N-\overset{CH_3}{\underset{CH_3}{C}}-CN}$$

Azobisisobutyronitrile (AIBN)

Especially since I was befriended with *Ibrahim*, I tried very hard to help him out of his dilemma, since none of the spectroscopic or other analytical techniques he had already applied had yielded any useful information. Neglecting my assignment for my own diploma, we jointly tried very hard identifying the respective structures of his 'poly(maleic anhydrides)' obtained either using AIBN, BPO, or pyridine as the polymerization catalyst. Unfortunately (or even fortunately in retrospect), the 60 MHz ^{1}H-NMR of solutions of neither specimen yielded any clue, since the lines were extremely broad and impossible to differentiate. The spectra reminded us of a cross-section of a nearby mountain range, called the 'Siebengebirge', a set of seven mountains of volcanic origin in the vicinity of Bonn.

Interestingly though, the two starting materials for his recipe, namely both AIBN and maleic anhydride (MA) gave rise to one sharp resonance line each in the ^{1}H-NMR spectra, and this triggered the thought that perhaps at early stages of their conversion, *i.e.*, during the polymerization, it ought to be possible to obtain still sharper lines, *i.e.*, 'better resolved' spectra.

Therefore, we followed the onset of the polymerization of a mixture of plain, and originally solid, MA and AIBN *in situ*, namely by setting the temperature within the NMR probe to 100 °C and thereby melting and inducing the reaction upon the warm-up within the NMR probe.

Much to our surprise, we did not only obtain just sharper or well resolved lines, but huge intensities thereof. We quickly recognized that some of these humongous lines were upside down, *i.e.*, either they occurred with an inverted phase or perhaps even in emission! – In striking difference to this result – or to an essentially similar one obtained when using BPO as the initiator, – was the lack of any such 'action', when polymerizing MA using pyridine. In this case, the sharp lines of the starting material would just disappear, and the broad and unrevealing resonances of the polymer did grow in.

Even though this gave us a clue of some sort, this 'spectacle' was far above the capacity of our comprehension. Frustrated accordingly, my friend *Ibrahim* remarked in despair: 'Before, I just did not know what I had, but now I don't even know, what you are doing there! – I thought I just had enough problems before, but now I even have some more!' – From then on, I was all alone.

'If fate gives you a lemon, make lemonade', recommends a well-known saying, but just how to do that in such a situation is not revealed by this recommendation. – Well, there was a (faint – in my opinion) chance that the time-proven *Varian* spectrometer just 'misbehaved', at least that was the dominating opinion of other colleagues in the Institute that I confronted with this finding. Therefore, I took all the required components for my experiments to the Institute of Organic Chemistry in an adjacent building, who owned a *Perkin-Elmer* NMR spectrometer based on a paramagnet and was using just one single radio frequency coil instead of the separate transmission and receiver coils of the *Varian* approach. The results obtained as a guest operator using the *Perkin-Elmer* machine were essentially the same, however!

Another draw-back of this phenomenon, or at least of the mode, in which we had previously conducted the experiments, was the short duration of the spectacle: Typically, it was all over in a matter of seconds or at best of minutes. – It is worth pointing out that in these days of analog NMR spectrometers, there was no field-frequency lock available at our spectrometer, and hence it was very tedious to even pinpoint the likely position of these resonance lines, not even to attempt to assign their identity to a likely chemical structure or even functional group.

Even though the spectrum at the start contained just two sharp *singlets*, the matter became very complicated upon the onset of the reaction, and the whole spectroscopic range between 0 and 8 ppm was full of these most intense resonance lines, some pointing up indicating absorption, others pointing downward signaling emission! Reducing the temperature did slow down the process some, but it also reduced the intensities of the mysterious lines such that this represented no remedy.

NMR spectrometers of this vintage typically contained no computers for any purpose what-so-ever but used a frequency modulation of the external magnetic field operating at about 2 kHz in combination with a lock-in detection of the resonance absorption. In principle, this ingenious but somewhat complicated mode of detection for the sake of noise reduction had its virtues, but it also had considerable drawbacks, since in there could have been hidden a source of signal distortion such as shifting the 'phase' of the resonance lines. Having ruled out this possible complication or culprit by means of the 'guest experiments' at the *Perkin-Elmer* spectrometer, there was a unique chance imbedded in this field-modulation concept: It suddenly occurred to me that if I recorded both the modulated signal and the reference frequency of the lock-in amplifier simultaneously on the two separate tracks of a stereo-tape recorder, I could lower the speed of the tape and feed the two channels thereafter back into the usual lock-in amplifier of the NMR spectrometer (*Fig. 3*). This concept allowed me to slow down the speed, with which the 'spectacle' occurred, thereby extending the time of its duration. This approach worked indeed surprisingly well and did not cause any severe distortions of the recorded information, as long as the change of the tape speed was not too dramatic. This in turn challenged me to file a patent on my own with little outside help on this more general concept of a 'slow-motion observation of chemical reactions' that I was awarded and which I subsequently sold to the German *Siemens* Corporation, who never used it to the best of my knowledge. – (My originally recorded two-track magnetic tapes still exist!)

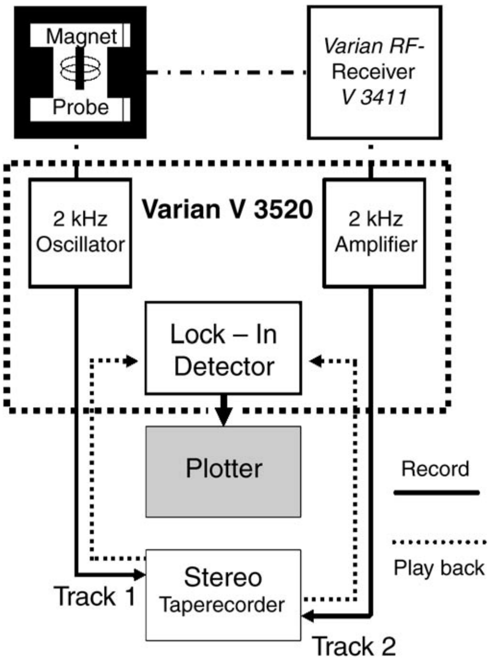
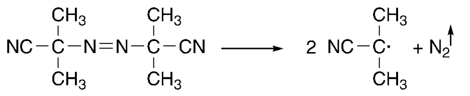


Fig. 3. *Schematic representation of a device to follow reactions in slow motion*

Both the systems MA plus either AIBN or BPO turned out to be far too complex and not suitable to be understood in any way; therefore, I started to search for other, hopefully simpler systems that would show a similar phenomenon.

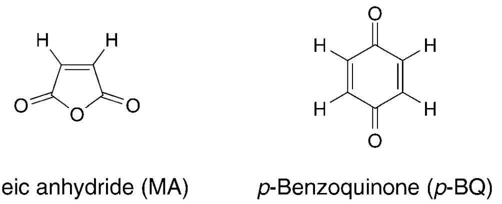
At that stage of my quest I simplified the experiment using just AIBN alone and no MA nor any solvent nor anything else as an additive or potential reaction partner. Much to my very surprise, however, I observed nothing unusual in this case: Just a decrease of the AIBN resonance line and a built-up of those of the decomposition products (see *Scheme*). – This result had serious negative consequences for my own original concept to explain my observations: I had thought that free radicals were to 'blame' for the occurrence of the strange lines in the *in situ* recorded NMR spectra, but then the decomposition of AIBN just by itself should have given rise to a related phenomenon. – I did not dare to decompose BPO as a solid by itself, a peroxide after all, – in the probe of the NMR spectrometer due to my fear of a potential explosion. – Hence an additive of some strange property seemingly had to be present during the decomposition of AIBN to reveal any unusual phenomenon, but what type with what kind of property did it have to be?

Scheme.*Decomposition of AIBN into 2 Free Radicals*



$$NC-\underset{CH_3}{\overset{CH_3}{C}}-N=N-\underset{CH_3}{\overset{CH_3}{C}}-CN \longrightarrow 2\ NC-\underset{CH_3}{\overset{CH_3}{C}}\cdot + N_2\uparrow$$

Studying physics, I was impressed by symmetry already early on and by the power thereof to extrapolate to related systems. Accordingly, I 'symmetrized' maleic anhydride in my very own special way, *i.e.*, I searched for another symmetric compound of related structure and arrived at *p*-benzoquinone (see *Fig. 4*), which I considered to be a 'close structural relative' of MA and potentially an alternate mate for either AIBN or BPO in my NMR experiments.



Maleic anhydride (MA) *p*-Benzoquinone (*p*-BQ)

Fig. 4. *'Structural relatives' and reaction partners for azobisisobutyronitrile*

My joy was great finding out that this concept – no matter how shaky or even wrong, – worked indeed, because now I had more flexibility and alternatives to explore the strange phenomenon with. However, the reaction of *p*-benzoquinone (*p*-BQ) and AIBN, albeit seemingly much simpler, did not gain me much progress. It too was beyond my comprehension at that time (and it seemed that I was in good company when discussing it with others).

When trying to figure out, what MA and *p*-BQ have in common chemically, it occurred to me that they are both good electron acceptors. Therefore, I went to the stock room of chemicals in our Institute and got aliquots of all those on board: They all worked in one way or another when combined with AIBN, for example!

Unfortunately, neither I nor anyone I asked knew at that time, in which way free radicals react with electron acceptors. Therefore, even this semi-success turned out to be a bottleneck.

Having no apparent other alternatives left, I then decided to investigate the decomposition of dibenzoyl peroxide in a solvent. Using cyclohexanone for that purpose, which I typically used as my favorite solvent for PVC, which I was supposed to study, I soon recognized that one of the decomposition products of BPO, namely benzene, occurred in emission rather than in absorption (*Fig. 5* and *6*). Likewise, when using *p*-dichlorobenzoyl peroxide, I obtained chlorobenzene in emission as well. Unfortunately, no other suitable peroxides were available except diacetyl peroxide, to which I will come back later.

As a future physicist, I had not acquired the skill to synthesize other peroxides myself, and I rated this endeavor to be too dangerous in light of my limited experience or even complete lack thereof in synthesizing chemicals as tricky as those. Therefore, I consulted a few catalogs of various chemical manufacturers, and I found out that a company called '*Elektrochemische Werke Höllriegelskreuth*' in the vicinity of Munich would

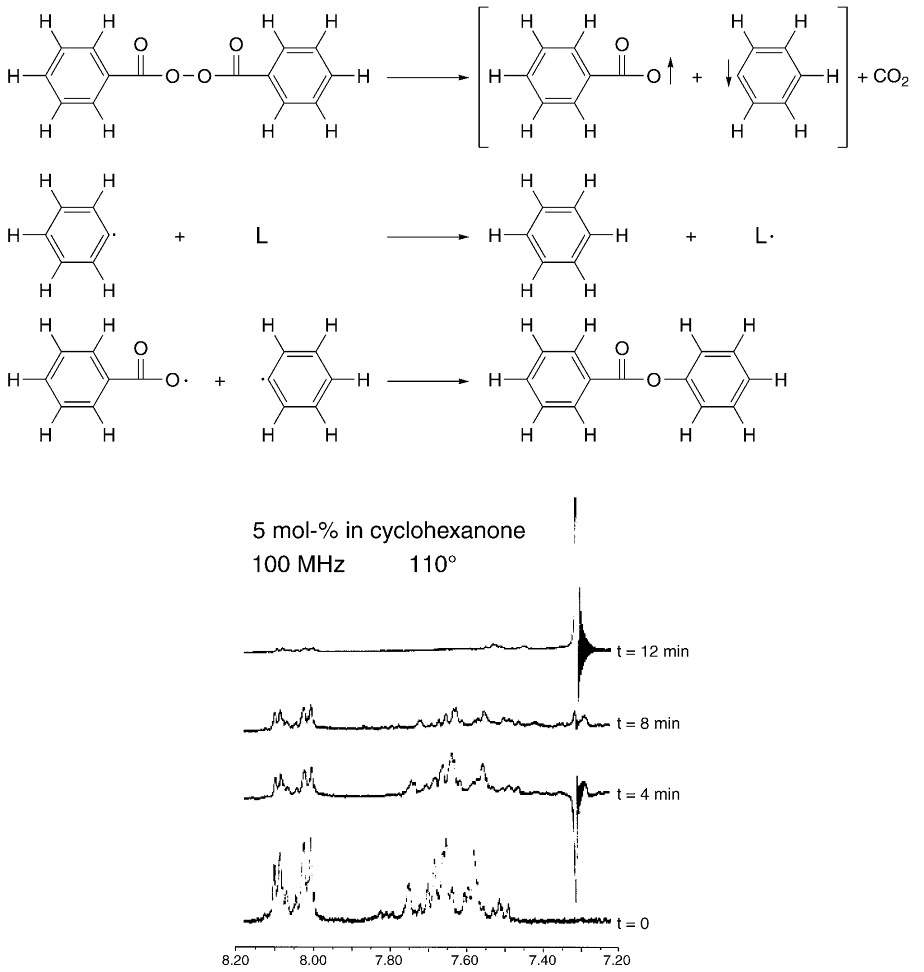


Fig. 5. *Decomposition of dibenzoyl peroxide and NMR spectra observed during the reaction*

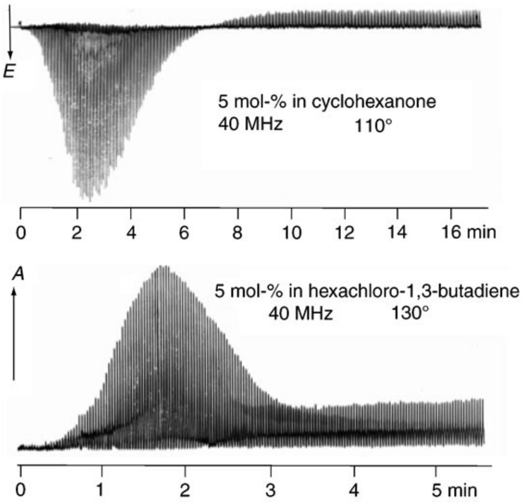


Fig. 6. *Time dependence of the emission of benzene during the decomposition of BPO in cyclohexane* (top) *and of the phenyl end groups during the thermal cleavage of BPO in the presence of methyl methacrylate* (bottom)

make such peroxides but required that I would pick them up there, because of their limited stability and sensitivity to above room temperature.

Knowing no other convenient alternatives I, therefore, waited for a cold winter day with temperatures below freezing and used my private car accompanied by my wife to pick up the requested peroxides at this place close to Munich. Fastening the sensitive material packaged in a cardboard box to my rear bumper of my vintage 1961 *Ford*, I made sure not to spend too much time on Germany's Autobahn and arrived safely at Darmstadt with my precious compounds. Among them were dipropionyl peroxide and other homologues. However, the study of these additional peroxides yielded new information, but no conclusive insight into the physics behind the strange phenomenon.

The study of the decomposition of diacetyl peroxide had even seemingly detrimental consequences, fortunately not due to a likely explosion, but pertaining to my efforts to establish a theory explaining the phenomenon, I had come up with in the meantime: Having observed benzene in emission namely, I had tentatively figured out that the product benzene might initially be formed in its *triplet* state and decay to its ground state thereafter, flipping or polarizing its nuclei in the process at the expense of relaxing its electron from *triplet* to *singlet* multiplicity. In this way, I reasoned speculatively, the system might conserve spin, and since the energy content of a system of unpaired electrons exceeds that of a nuclear system in the same external magnetic field, such a process might well be allowed energetically at least.

Whereas this concept could have been applied to benzene, whose *triplet* state exists, it could not apply to ethane or methane, the decomposition products of diacetyl peroxide. Therefore, upon observing both methane and ethane during the decomposition of diacetyl peroxide, ethane in emission and methane in enhanced absorption (see *Fig. 7*), my hypothesis could not possibly hold, since the *triplet* states of these two products are non-bonding.

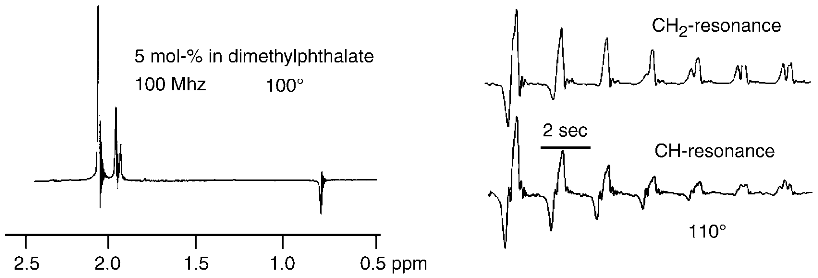


Fig. 7. *CIDNP of ethane* (in emission at 0.8 ppm) *and of methane* (in emission, not shown since outside of the depicted range to the left) *observed during the decompostion of diacetyl peroxide* (left) *and* multiplet *effect in* CH_2*- or CH-resonances of telomerization product during decomposition of BPO in the presence of styrene and* CBr_4 (right)

The decomposition of diproprionyl peroxide was even more puzzling: During its reaction, the resonances of its decomposition products showed what was later called the '*multiplet* effect', namely the occurrence of both emission and enhanced absorption within one and the same multiplet of a particular decomposition product such as ethyl chloride, when CCl_4 was used as a reactive solvent.

Fortunately for me, at about this time, a visitor, Dr. *Ellinger*, from the *ICI Corporation*, Great Britain, paid a visit to the German Plastics Research Institute. Dr. *Ellinger* was an expert on copolymerization of maleic anhydride with other monomers, in particular with acrylonitrile, which was used by *ICI* as a component of fibers based on poly(acrylonitrile) to render them colorfast after dying. Therefore, I had some lengthy conversation with him, trying to figure out how maleic anhydride behaves during copolymerization. Dr. *Ellinger* knew Prof. *Rex E. Richards* of Oxford University, (who became Vice-Chancellor of Oxford University in 1977 and was knighted in this context).

As a consequence of the ensuing conversation between Dr. *Ellinger* and Prof. Sir *Rex E. Richards*, the latter sent me a letter, outlining that long before my experiments he had thought of a way to induce the well-known *Overhauser* Effect chemically, *i.e.*, by breaking of a chemical bond. In this fashion, Sir *Richards* assumed, that a system should result with pairwise unsaturated electrons having an identical amount of spins aligned with and against an external magnetic field. This should correspond, he reasoned, to a system containing free radicals upon achieving saturation of the ensemble of electrons, just as if they had been pumped to saturation upon irradiating them with their resonance microwave frequency in a double resonance experiment. This type of *Overhauser* experiment had originally been predicted theoretically by *Overhauser* and shown later to work experimentally as well by *Carver* and *Slichter*. Prof. Sir *Richards* wrote: 'It would be more than a coincidence, – and hence not a surprise to me, – if what you have found by accident and what I had thought of previously is essentially the same thing!' In this fashion, without maybe knowing it consciously, Sir *Richards* coined the plausible expression '*Chemically Induced Dynamic Nuclear Polarization* (CIDNP)', which in German is '*Chemisch Induzierte Dynamische Kernpolarisation*'.

This acknowledgment of an experienced and important scientist changed the mind of my advisor, Prof. *Hellwege*, who had left me pretty much alone prior to this letter, being afraid I would blow up his precious NMR spectrometer with my suspicious chemical experiments. He had consistently blocked any effort or suggestion of mine, to publish my observations, since he did not believe in the fact that they were of any significance or value. Since before, I had no idea what the true origin of this phenomenon might be, he typically answered by underlining that he headed 'an honorable institute of physics, were we publish only what we know and understand': Since this did not apply in my case, I did not get his permission to publish or report my results.

In addition to this pleasing consequence, it had now become apparent that my observations in the field of NMR spectroscopy did not only involve processes of nuclei, but radical electrons also accounted for part of the action. This, however, was the domain of *Hanns Fischer*, who indeed had considerable experience, lecturing about ESR. Accordingly, he became interested in this matter immediately, and from then on we tried to explore and to exploit this novel phenomenon together (*Fig. 8*). We conducted experiments in the presence of paramagnetic salts, determined the enhancement at different spectrometer frequencies, and did some calculations jointly.

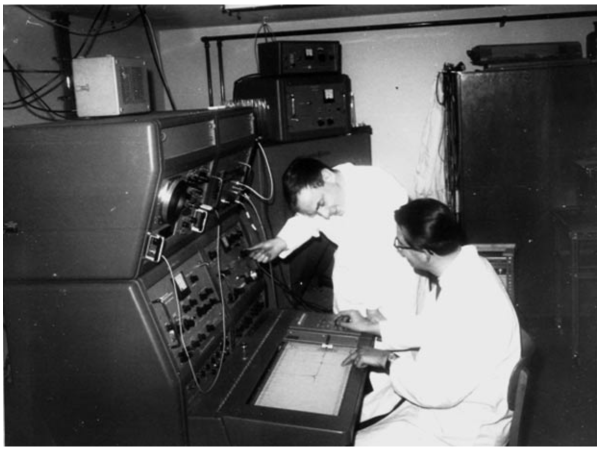


Fig. 8. *Introducing* Hanns Fischer *to CIDNP in front of our* Varian DP 60 *NMR spectrometer*

A generally accepted expert in Germany of Dynamic Nuclear Polarization (DNP), otherwise known as the '*Overhauser* Effect', was Prof. *Karl H. Hausser* of the Max-Planck Institute of Medical Research at the University of Heidelberg. Especially since Heidelberg is only a short distance away from Darmstadt, and because *Hanns* knew Prof. *Hausser* very well anyway, we decided to present our results to him and a graduate student of his, *Dietmar Stehlik*, who is now a physics professor at the Free University in Berlin. *Stehlik* and *Hausser* had written a review article on DNP and were otherwise very knowledgeable about anything in connection with the *Overhauser* Effect. They liked and rated our DNP-based explanation of CIDNP plausible, convincing and therefore highly likely to apply. Their positive reception of our presentation and an ensuing invitation to present our results at a related workshop on 'Polarization Phenomena in Magnetic Resonance', held in the late summer of 1967 at the '*Waldemar Petersen Haus'*, a retreat and conference facility owned by the Technical University of

Darmstadt at Hirschegg, located at the borderline between Austria and Germany, gave us the courage to finally publish our results in the literature.

As a suitable scientific journal to publish our results, we chose the German journal *Zeitschrift für Naturforschung*, in which *Hanns Fischer* had traditionally published his ESR results of his studies on a variety of free radicals. For this purpose, we divided up my studies into two parts, one describing my experiments, which I had done under the supervision of Dr. *Johnsen* and a second contribution about the (likely) interpretation thereof, in which Dr. *Johnsen* had no part. When getting my spectra and drawings ready for publication, war broke out in the Middle East, and in the process the Suez Canal became blocked, threatening Germany to be subjected to a shortage of gasoline. Since my family had made reservations in Switzerland and France to spend part of our vacations there, and since we had to get there by car with our two little children, I hastened to get everything ready for a swift departure as long as gas was still available. When I came to the Institute the morning of our intended departure to Switzerland, I found my spectra soaked in water dripping from the ceiling: Some graduate student in the Department of Chemistry located a flight of stairs just above my office had not wired the hoses for the cooling water supplying a reflux condenser. Upon their rupture, the cooling water had flooded the floor above my office and penetrated the ceiling, ending up on my printed spectra. This was absolutely disastrous, since in those days prior to the introduction of computers into NMR spectrometers, any printout was a unique original. Therefore, it seemed that everything I had done before may have been in vain. Fortunately, however the '*Pelican*' ink of a German manufacturer turned out to be waterproof, consequently there was a remedy, namely to iron the spectra with a steam iron, which I brought to the Institute from home. Fortunately, this approach worked out, and the spectra that we subsequently published have been ironed flat again carefully prior to their submission. Thereafter, I left in a hurry together with my family, and I left it up to *Hanns Fischer* to submit the two manuscripts to the publisher.

Upon my return from our family vacations, *Hanns* told me that he had attended the 1967 *Gordon* Research Conference on Magnetic Resonance at New Hampshire, USA, where he had been invited to deliver a presentation about his theory of the magnitude of hyperfine couplings of simple free radicals. Instead he had approached the chairman of this conference, telling him about the novel observations we had just written a paper about together. The chairman gave him permission to change his topic and disclose the results of our CIDNP experiments and hypothesis to explain our findings. Shortly after *Hanns* had started out showing our spectra and outlining the CIDNP concept, two other attendees of this *Gordon* Conference jumped up and confirmed that they had observed essentially similar phenomena during the reactions of alkyl halides with alkyl lithium compounds. Their names were Prof. *Ronald G. Lawler* and Prof. *Harold Ward*, both of Brown University, Providence, Rhode Island, in the US.

Lawler and *Ward* apparently liked our interpretation so much that they accepted the same title for their communication to the editor of the *Journal of the American Chemical Society*, namely 'Chemically Induced Dynamic Nuclear Polarization'. Our explanation of the CIDNP phenomenon did not fit to their results, however, since it could not explain what subsequently became known as the 'multiplet effect', namely the simultaneous occurrence of both emission and enhanced absorption within the same *multiplets* in virtually all of their spectra. This did not stop them from jumping the band wagon, however, and accepting our proposed theoretical interpretation.

Interestingly, both our and their publications appeared within the same months in the fall of 1967, ours in German in the *Zeitschrift für Naturforschung* entitled '*Kernresonanz-Emissionslinien während rascher Radikalreaktionen*', [2] and '*Chemisch induzierte dynamische Kernpolarisation*', [3] theirs in the *Journal of the American Chemical Society* with the title '*Chemically Induced Dynamic Nuclear Polarization: Evidence for One-Electron Transfers during Some Halogen-Metal Exchange Reactions*' [4].

The fact that our contributions were published in German and only had the summary in English did not help its level of recognition. Nevertheless, thanks to the contacts (and fairness) of *Lawler* and *Ward* to *Chemical and Engineering News (C & E News)*, the periodical for the members of the American Chemical Society, an article appeared in the January 15, 1968, issue [5], which highlighted the experiments of both groups jointly (*Fig. 9*).

Fig. 9. *Prof.* Ronald G. Lawler *of Brown University* (left), *Prof.* Harold R. Ward (center), *and the January 15 issue of* Chemical and Engineering News

The timing of this article in *C & E News* could not have been any better, because a well known German Newspaper, *Frankfurter Allgemeine Zeitung*, contacted us at Darmstadt and requested some information of our supposed discovery of a 'RASER', which according to *C & E News* should generate radiofrequency radiation in similarity to a LASER but in our case from a chemical reaction. This article in turn became known to another German newspaper, albeit on the other side of the Iron Curtain, namely in Leipzig, located in what was then still part of the *German Democratic Republic*, in short the DDR for *Deutsche Demokratische Republik,* otherwise referred to as '*East Germany*'. The article that was published in Leipzig was shorter but otherwise like that of the *Frankfurter Allgemeine Zeitung (FAZ)*.

Long before this unexpected publicity of my (still somewhat puzzling) research results namely, the date for my oral defence of my Ph.D. thesis together with my oral examination *('Rigorosum')* in presence of the Science Faculty of the Technical University of Darmstadt – required for obtaining a Ph.D. degree in physics at that time – was set for February 14 in 1968. Thanks to these newspaper articles, in particular that of the

FAZ, I had no difficulty explaining to the Science Faculty of my university what I had done and accomplished during my graduate studies at the German Plastics Institute: They all pretty much knew it already by then. My oral exam was not any easier though, but I got out of there with my Ph.D. degree having passed with the best possible grade. Accordingly, I owe a belated 'thank you' to *C & E News*, the *Frankfurter Allgemeine Zeitung*, *Hanns Fischer* and all the other colleagues mentioned above, who had encouraged me and/or contributed to the publicity of the topic of my Ph.D. thesis, the first thesis with title 'Chemically Induced Dynamic Nuclear Polarization' (in German: '*Chemisch Induzierte Dynamische Kerspinpolarisation'*). – Another thesis by somebody else with more or less the same title was yet to follow as outlined below.

From this point on, I was a member of *Hanns Fischer*'s group in capacity of a postdoctoral fellow. By then, another new graduate student had joined the ESR Group of *Hanns*, namely *Manfred Lehnig*, a young physics major with interests similar to my own. He picked up the topic of CIDNP as well and continued to complete the then accepted theory where *Hanns* and I had left it, especially by devoting more attention to relaxation phenomena. In addition, two new rookies joined *Hanns*' group, namely two other physics majors, who immediately before had served in the army, however, for two years due to the draft. One of them was *Bernd Blank*, who by now has passed away much too early. When I introduced them to the world of CIDNP, warning them to be particularly careful when dealing with peroxides, they laughed and pointed out that in contrast to me they had accumulated a lot of hands-on experience in handling explosives during their service in the German army called '*Bundeswehr*'.

It did not take long, however, when a formidable explosion rocked the Institute, because these two new members of *Hanns*' group had disregarded my warning and triggered an explosion within the probe of our *Varian DP 60* NMR spectrometer. Prof. *Hellwege*, the 'big boss' of the Institute as he was commonly called, was livid. He had always been very wary and uneasy about my chemical experiments in his beloved spectrometer, and now he had the expected proof of the pudding. Fortunately, nobody had been hurt, and as it turned out, this mishap had even a good side: The German Plastics Research Institute is a private organization at the Technical University of Darmstadt and not a genuine institute of the University itself. Therefore, it had to carry insurance for bodily injury of its people and for the equipment, in contrast to the practice at genuine University Institutes that are owned and operated by the State, which insures itself as a big enough entity. Consequently, we took advantage of the damage caused by the explosion and upgraded our *Varian DP 60* NMR spectrometer to a more powerful *Varian HA 100*, operating at the then practically top-of-the-line ^{1}H resonance frequency of 100 MHz, not to mention other significant improvements. – Accordingly, even the 'big boss', Professor *Hellwege*, was again calmed down and finally satisfied.

Professor Sir *Richard*'s suggestion that the physics behind the emission and absorption lines, which since then has become known as 'CIDNP', was related to or based on the *Overhauser* Effect (hence 'DNP'), seemed to be applicable to our results, where all lines of a given multiplet occurred either in emission or all in absorption. It failed completely, however, to explain the '*multiplet* effect', which dominated the results of *Lawler* and *Ward* and occurred in some of our experiments as well. This fact caused me some headaches, since I knew intuitively that the state of the affairs was still unsatisfactory. However, the systems that were accessible to me experimentally were rather complicated and not particularly suited as simple model systems to test out alternative concepts for explaining for example the *multiplet* effect as well.

My limitations resulted for a considerable part from my lack of knowledge, experience, and skill in chemical synthesis or in alternate concepts to generate free radicals at will such as *via* photochemistry.

Therefore, I made an effort to learn more chemistry, if possible as postdoctoral fellow in an American Research Lab or university. Accordingly, I sent a bunch of query letters to a few people, whose research I knew from the literature. Among them was Prof. *George S. Hammond* at the California Institute of Technology (Caltech) at Pasadena, California, in the US. Much to my most pleasant surprise, he responded very positively to my inquiry whether I could learn the basics of organic chemistry and photochemistry in his group in exchange for injecting some ideas of what later became known as 'spin chemistry' into the knowledge portfolio of his group. *George S. Hammond* (see *Fig. 10*) had begun his academic career at Iowa State University in 1948, moving to Caltech in 1958. At Caltech, he continued investigating the mechanisms of free radical and ionic reactions, and he had also launched a program in photochemistry that he had begun in Iowa as well. Between 1960 and 1963, *Hammond* and his co-workers had published the work that led to the creation of organic photochemistry as an academic discipline. Many years later, in recognition thereof, he was awarded the 1994 Medal of Science, the Unites States' highest science award for 'virtually creating the field of organic photochemistry'.

Before leaving for the United States in February of 1969, I stayed in *Hanns Fischer*'s group as a postdoctoral fellow and explored the then still novel CIDNP phenomenon in more detail. In line with the research mission and interests of the German Plastics Institute, I investigated polymerization reactions induced by both dibenzoyl peroxide and AIBN. The results differed characteristically, if BPO was decomposing in either a relative inert solvent (for example in hexachloro-1,3-butadiene), in a reactive solvent like hexachloroacetone, or in the presence of a vinyl monomer like styrene [6].

Fig. 7 shows some of the CIDNP spectra and the time dependence of the emission or enhanced absorption lines, respectively, recorded during the reactions. The results thereof did not disagree with the DNP-based explanation of CIDNP that we still adhered to at the time, but if a reaction yielded the *multiplet* effect in one of the reaction products, that was beyond the end of our rope.

Knowing that the DNP-based theory had serious limitations or even more general problems, I took advantage of a visit of Prof. *J. H. van der Waals* (see *Fig. 10*) from the University of Leiden in the Netherlands to discuss with him some of the grievances I still had with the state of the affairs of CIDNP. Prof. *van der Waals* had published a book on the *triplet* state of organic molecules. Since I had blamed the *triplet* state of benzene early while trying to explain the NMR emission lines of benzene observed during the decomposition of BPO on my own, I was keen to extract some clues or information out of him with respect to the potential role or significance of the *triplet* state in CIDNP-showing free-radical reactions.

Even though this conversation in Darmstadt did not immediately reveal any new insights or results, it lead to progress in the long run, albeit not so much in Darmstadt, but in Leiden (NL) and likewise, – whereby the details are still unknown to me, – in parallel in Chicago in the US.

Fig. 10. G. S. Hammond (Caltech), J. H. van der Waals (Leiden), R. Kaptein (Leiden/Utrecht), G. L. Closs (Chicago), R. W. Fessenden, *and* R. H. Schuler (Mellon/Notre Dame)

Upon his return to Leiden University, namely, Prof. *van der Waals* told his colleague, Professor *L. J. Oosterhoff* (1907–1974), likewise of the University of Leiden (NL) what he had learned and seen in our Institute in Darmstadt. As a result of this conversation, Prof. *Oosterhoff* appointed a new graduate student, *Robert Kaptein* (see *Fig. 10*), to repeat most of my experiments and thereby build a knowledgebase of their own. Accordingly, during the early stages of his time as a graduate student in Prof. *Oosterhoff*'s group, *R. Kaptein* synthesized a variety of diacoyl peroxides and investigated the thermally induced decomposition of some of these radical generators in considerable detail. In their first joint publication of these experiments in *Chemical Physics Letters*, *Robert Kaptein* mentioned in a footnote that he interpreted his results based on the then prevailing theory, but he clearly underlined his concerns about the validity of this theory and his serious doubts by stating ‘or whatever it may be’ [7].

Simultaneously and totally independently, – and unknown to both us in Darmstadt and the team in Leiden, – Professor *Gerhard L. Closs* (see *Fig. 10*) used some ideas of his own launching a program in parallel together with his graduate student *Alex Trifu-*

nac trying to shed some more light into the still somewhat mysterious CIDNP phenomenon. *Closs* had a sizable knowledgebase in organic chemistry, in particular of carbenes and the reactions of organic intermediates, both in their *triplet* or *singlet* states, which he now used to his advantage in designing a set of clever and revealing experiments to elucidate the true physical basis of CIDNP.

At the time when I left Europe with my family in February of 1969, crossing the Atlantic Ocean by boat and the continental United States by car coast to coast from New York to Los Angeles to start my postdoctoral fellowship at Caltech at the end of March in 1969, neither group had revealed novel findings pertaining to the physics or the theoretical explanation of CIDNP. This occurred later during my time as a postdoctoral fellow in *George Hammond*'s group, where I had started to synthesize partially deuterated precursors for the photochemical generation of (hopefully) simpler model systems to check and/or augment the then existing concepts of the mechanism causing CIDNP. Learning the basics of wet organic synthesis from other postdocs in the *Hammond* Group and at the same time the rules and facts of photochemistry and photophysics, I made considerable progress filling up my gaps in the knowledge of physical and organic chemistry. Nevertheless, the other two groups had already received the correct ideas, and the results thereof were published by both groups more or less simultaneously later in 1969 in the *Chemical Physics Letters* by *Kaptein* and *Osterhoff* and in the *Journal of the American Chemical Society* by *Closs* and *Trifunac*, respectively [8][9].

Either contribution had identified what subsequently became known as the 'radical pair model', a theoretical concept, which for the first time could even account for the previously puzzling '*multiplet* effect'. Early gaps or original shortcomings of these two related albeit independently perceived concepts and derived conclusions, like for example the role of the *g*-value of the individual radicals within the radical pairs, were quickly augmented, and the 'childhood diseases' were soon remedied in subsequent publications of both groups.

By now, this 'radical pair concept' is generally accepted, whereas the DNP-based explanation of CIDNP has been discarded. Furthermore, by now, the radical pair concept is a vital module of what later became known as 'spin chemistry' [10][11].

Even prior to our or *Lawler*'s and *Ward*'s 'pioneering' CIDNP experiments, other researchers had observed similar phenomena in NMR spectra recorded *in situ* during chemical reactions, possibly with or without paying attention to it. Among those is for example Professor *Christopher Rappe* of the University of Umeå in Sweden, who told me later about his earlier puzzling observations. Seemingly, however, he had not noticed the attractive potential hidden in his 'strange observations', and it is quite likely that other researchers had similar 'encounters'.

Likewise and yet unrelated, an essentially similar phenomenon had been observed long before the first CIDNP evidence, namely already in 1963 in ESR spectra recorded during pulse-radiolysis initiated cleavages of a variety of compounds by *Richard W. Fessenden* (see *Fig. 10*) and Professor *Robert H. Schuler* (see *Fig. 10*), now at Notre Dame University. This group had published their results in the *Journal of Physical Chemistry* [12], but the fact that some of the ESR lines appeared in emission had virtually gone by unnoticed by the magnetic resonance community, until the discovery of CIDNP and the unravelling of its physical basis made it timely and feasible to reinvestigate this related

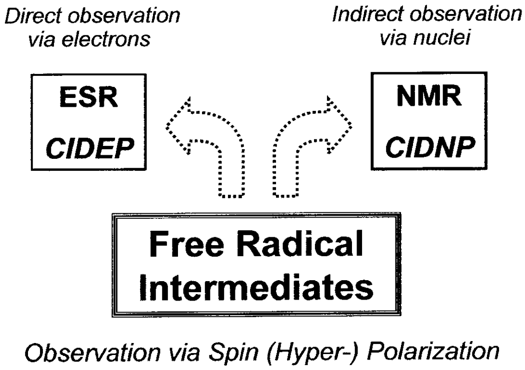


Fig. 11. *CIDNP and CIDEP in comparison*

phenomenon, which marked the onset of the existence of Chemically Induced Dynamic Electron Polarization (CIDEP) (*Fig. 11*).

Apparently (and as outlined by *H. Hayashi* [10]), a similar observation of what may have been CIDEP had been made in 1965 by *Y. Kurita* at the Basic Research Laboratory of *Toyo Rayon Co.*, Ltd., in Japan, but it passed virtually unnoticed.

In any event, *R. W. Fessenden* is regarded as obtaining the first evidence for the CIDEP phenomenon [12]. He had received his Ph.D. in 1958 at the Massachusetts Institute of Technology (MIT). Thereupon, his research interests included for example reactive intermediates in radiation and photochemistry, the structure, reaction mechanism, and kinetics of radicals, radical ions, and excited states, which he studied by ESR and optical methods. Augmented by CIDEP, he, therefore, was a perfect match and host to accommodate *Hanns Fischer* for a sabbatical which he was about to spend in the US. *Hanns*' time with *Dick Fessenden* and Prof. *Robert H. Schuler* at the Radiation Research Laboratories of the Mellon Institute, Carnegie-Mellon University, Pittsburgh, Pennsylvania, USA in 1969, established a close personal friendship especially between *Hanns* and '*Dick*' *Fessenden*. It was there, where *Hanns Fischer* wrote a review article on CIDNP for *Accounts of Chemical Research* [13] still pretty much unaware of the 'uprooting' developments in both Leiden and Chicago.

Having returned from Pittsburgh, *Hanns Fischer* was appointed as professor of physical chemistry at the University of Zurich (CH), to where he took some of his group from the Technical University of Darmstadt, including *B. Blank* (the 'explosives expert'), *M. Lehnig*, and *H. Paul*. There, he established a group that was to become quite sizable in the years to follow, devoted to research in both optical and magnetic resonance spectroscopy. With respect to the latter, he focused on polarization phenomena like in CIDNP, but he also continued his work in EPS spectroscopy and even in other, totally different fields.

1970 brought about additional contributions both by the previous and by new authors to the still emerging field of Chemically Induced Magnetic Polarization, in particular to the theory explaining CIDNP. These contributions came from the group of *Closs* [14], from *Hanns Fischer* himself [15], and in particular from *F. J. Adrian*, who had incorporated and accounted for the diffusion behavior of the radicals in much better detail and scrutiny [16]. Shortly thereafter, in 1971, *Robert Kaptein* had formulated simple and very handy rules to draw quick conclusions from the so-called 'phases' of the resonance lines in CIDNP spectra, – *i.e.*, whether lines appear in emission or absorption, which became known and subsequently quite popular due to their convenience as the '*Kaptein* (Phase) Rules' of CIDNP [17]. Subsequently, he again augmented the knowledgebase of CIDNP considerably [18].

In 1971, the Belgian Chemical Society conducted a workshop at Brussels, where *R. G. Lawler* and *G. T. Evans* [19] presented their concept and results that the course of chemical reactions involving radical pairs may depend on the occurrence of magnetic *versus* nonmagnetic isotopes in the pairs. These two authors had applied their concept differentiating light atoms like ^{12}C and ^{13}C, for example. Due to the dependence of intersystem crossing on nuclear spins, namely, a magnetic isotope effect, can be used to advantage to separate isotopes on the basis of nuclear spins rather than nuclear masses.

This concept originally applied 'harmlessly' to the separation of ^{12}C and ^{13}C, must have been extrapolated early on to the potential discrimination if not separation of ^{238}U and ^{235}U by a Russian (then Soviet) team, including *A. L. Buchachenko*, *Y. N. Molin*, *R. Z. Sagdeev*, *K. M. Salikhov*, *and E. L. Frankevich* (see, *e.g.*, [20]).

By 1972, the community interested in magnetic polarization phenomena such as CIDNP and CIDEP had grown considerably. Quite a few members of the then still young scientific community, including *Hanns Fischer*, – as well as *B. Blank* and *M. Lehnig* of his group in Zurich, – followed the invitation of an organization committee headed by Prof. *Endel Lippmaa* of Tallinn, which by now is the capitol of Estonia, one of the Baltic States, re-established after the dissolution of the former Soviet Union. At that time of the 'Cold War', namely in 1972, Estonia was still a Soviet Republic of the Soviet Union. For most scientists from the West, it was the first opportunity to meet colleges from the East, which all shared common scientific interest. As far as I am concerned, – among many others, – I got to know Prof. *Anatolii L. Buchachenko* from Moscow in Tallinn for the first time there.

Having completed my postdoctoral fellowship at Caltech at the end of March in 1970, I had joined the *IBM* Research Division initially as a postdoc at the *IBM* Watson Research Center in Yorktown Heights, New York, USA. In the summer of 1971, *IBM* decided to concentrate its scientific staff members devoted to basic research in chemistry at the by then considerably enlarged Research Laboratory at San Jose, California, USA, *i.e.*, in '*Silicon Valley*'. To stay and work in the US as a foreigner, *i.e.*, as German citizen, I had a permanent visa, otherwise known as a 'green card'. This type of visa became invalid, however, during the days of the 'Cold War', when its holder visited a Soviet-controlled foreign country. In order to be permitted to re-enter the United States required a so-called 'Re-entry Permit', which was granted upon request by the US Immigration Service upon filing a rather detailed explanation describing the reasons for and circumstances of an intended visit and associated trip abroad. I filed such a request and was granted a Re-entry Permit with no noticeable problems.

Having returned from this very exciting symposium in Tallinn, while conducting research again in the *IBM* Research Laboratory at San Jose, I received a telephone call one day at my office from the receptionist of the Lab telling me that two people had come to her desk wanting to talk to me. Strangely, however, they did not want to identify themselves, and since I did not expect any visitors on that day, I was tempted to decline their request. Thereupon the receptionist told me on the phone that these two people were 'representatives of the American Government'. They came in response to my visit to the Soviet Union and my request of a Re-entry Permit.

In the ensuing conversation, they tried to figure out in more detail, why I had been invited to Tallinn, why I had been offered reimbursement of my local travel expenses as long as they occurred in Soviet currency, and what I had been presenting and talking about with other colleagues in particular. Obviously, they were dissatisfied with my answers and explanations, because after nodding with their heads after some of my non-revealing statements one of them asked me straightforwardly: '*Are you that naïve or are you trying to pretend?*' Since I did not have any clue, what he meant or wanted, I had to confirm to him that I was that naïve! He, therefore, got more specific, asking whether I had met a certain Professor *Buchachenko*. Of course I had, but the Estonian organizers of the symposium had made an effort to subdivide the scientists from the West and those of the former Soviet Union such that the guests from the West formed a subgroup just with the Estonian scientists, whereas those from 'Russia' formed another subgroup. Technically that meant that the subgroup of the visitors from the West were taken to a sauna; we filled the associated social area to capacity when joined by the Estonians and some of their family members. The 'Russians' instead were sent to a local theatre, where they attended a guest performance of some well-known Russian ballet. The next day, other than during the presentations and posters, a similar thing happened in so far, as the subgroup of the visitors and the Estonians host entered a sailing yacht, borrowed from some function of the Soviet Republic of Tallinn. Coincidentally, this yacht just happened to be too small to accommodate all conference participants; therefore, the 'Russian' fraction had to use a large barge, which accompanied the sailing yacht alongside at some safe distance. Not surprisingly, in retrospect at least, Prof. *E. Lippmaa* became a member as a minister of the post-soviet Estonian Government. Because of these and similar 'precautions' by our Estonian hosts I had to disappoint the two 'Representatives of the American Government' in not having learned anything nor revealed any information about potentially separating ^{235}U from ^{238}U on a magnetic basis. The two 'Representatives' had to accept my naïve ignorance, but they warned me to be especially careful, should I meet Prof. *Buchachenko* or other members of what they referred to as the 'Russian Uranium Team', and they particularly discouraged me to visit the then Soviet-controlled German Democratic Republic. *i.e.*, East Germany.

Actually, I have met Prof. *Buchachenko*, – whom I respect very much as a colleague and scientist, – again in Moscow and in Novosibirsk thereafter in 1978 and subsequently, carefully avoiding discussions about the discrimination of separation of ^{238}U and ^{235}U magnetically rather than on a mass basis. We did talk about the discrimination of tin isotopes instead, however. After the end of the Soviet Union, Prof. *Buchachenko* and his team have published various articles, revealing their results [21]. I am still somewhat apprehensive to learn and understand everything what they have found.

Nevertheless, I was very impressed that these 'Representatives of the American Government' knew CIDNP even in 1972, and the level of their understanding the concepts and implied possibilities was remarkable.

Personally, I hope that the discovery of CIDNP will only be applied in a peaceful mode, such as has been practiced by the just retired Prof. *R. Kaptein* at the University of Utrecht and by his academic off-springs [22], but it should not contribute ever to anything that should better never happen. *Hanns Fischer* shared with me that same conviction.

This article is dedicated to the late Prof. *Hanns Fischer*, who is sadly missed by all of his friends and the scientific community of physical chemists and physicists who owe him a lot of credit and thanks for his numerous contributions, especially to the field of magnetic resonance spectroscopy, to single out just the very field in which our interests and careers overlapped for so many years. In particular, I owe him a lot of thanks for being a great teacher and a very skilled 'minister of foreign affairs', publicizing my originally quite hidden observations of an initially unknown and hence suspicious nature at first within Germany but then thereafter in the United States as well. Without him, I most likely would not have been able to accomplish anything similar.

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