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The reaction of $[(\eta^5\text{-cyclohexadienyl})\text{Fe}(\text{CO})_3]^+\text{BF}_4^-$ with 2-methyl-2-nitrosopropane: an unexpected oscillating reaction

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Abstract

The reaction of 2-methyl-2-nitrosopropane with the organometallic cation $[(\eta^5\text{-cyclohexadienyl})\text{tricarboxyliron}]^+$ yields the bis(*t*-butyl)nitroxide radical which is detected by ESR spectroscopy. The intensity of the ESR signal varies in an oscillatory manner with time and the ESR silent period between oscillations ranges from 15 minutes to one hour, depending on the relative concentrations of the reagents. Some years ago, Turcsanyi proposed (*Acta Chim., Acad. Scient. Hungar.*, 110 (1982) 305, *Chem. Abs.* 97 188877w) that a R–N=O/R–NH–OH system might exhibit oscillatory behaviour and the data presented are an experimental realization of that prediction. A mechanistic rationale is proposed to account for the observations.

Introduction

Oscillating chemical reactions [1] (especially those which involve dramatic colour changes) have attracted considerable attention in recent years not only because of their intrinsic beauty and visual fascination but also because they pose challenging problems to kineticists. As exemplars of non-linear processes they are also relevant to biological problems related to the formation of dissipative structures, to morphogenesis and to the growth of organisms [2]. The actual oscillatory reactions occurring in biological systems are, however, in general poorly understood and not closely related to the systems studied by inorganic chemists.

Many of the commonly demonstrated reactions are derived from the now classic observations of Belousov, Zhabotinski and their colleagues such as the reaction of bromates with malonates in the presence of a ferrous/ferric redox system [3]. Since that time, a number of variations on this theme have been developed and designed oscillatory chemical systems are now possible [4]. However, our involvement in this field was entirely serendipitous.

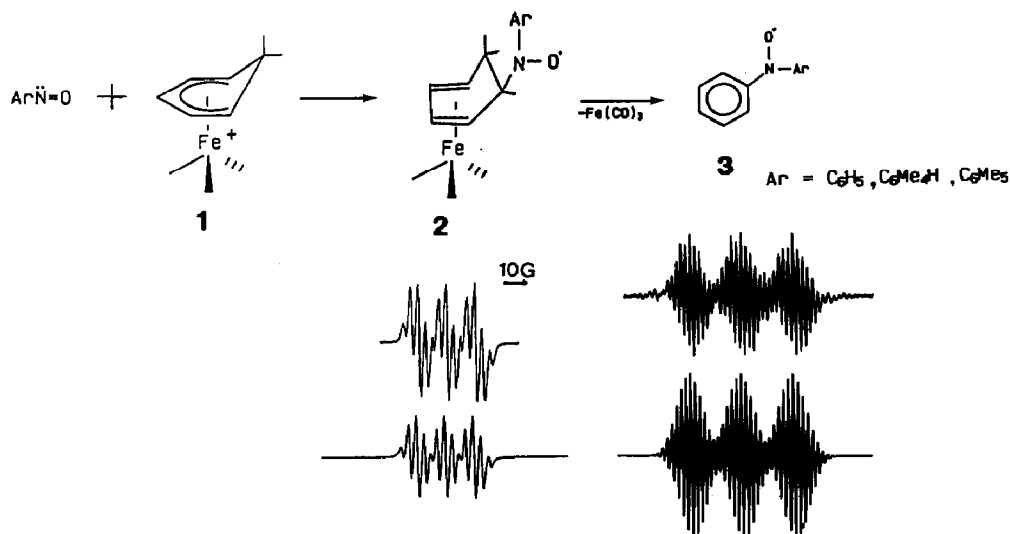
In continuation of our ESR studies [5] of organometallic nitroxide radicals derived from the interaction of metal carbonyl stabilized cations such as **1** with

nitrosoarenes (which give organometallic nitroxides **2** and diarylnitroxides **3**), we treated the cation $[(\eta^5\text{-cyclohexadienyl})\text{Fe}(\text{CO})_3]^+$, **1**, with $t\text{-BuNO}$ with the expectation of observing the simple radical **2**. However, the ESR spectrum exhibited as its major feature a simple triplet signal readily attributable to the well-known bis(t -butyl)nitroxide radical, $(t\text{-Bu})_2\text{N-O}\cdot$. Even more surprising was the observation that the intensity of this triplet resonance showed oscillatory behaviour with time. We here describe a set of experiments in which we attempt to delineate the factors controlling the formation of the various radical products. We also note the very different rates of oscillation when the concentrations of the reactants are changed.

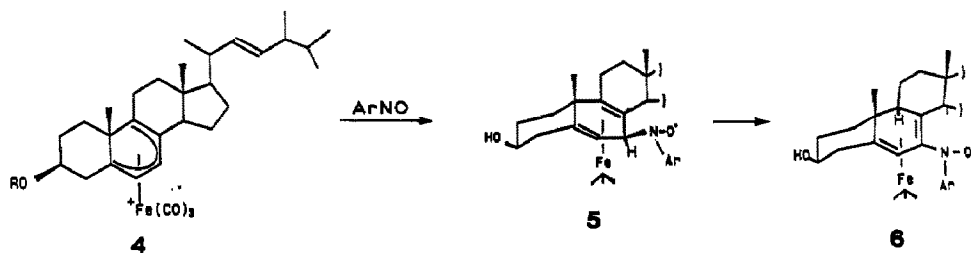
Results and discussion

We have recently reported [5] that the reactions of nitrosoarenes with the $[(\eta^5\text{-cyclohexadienyl})\text{Fe}(\text{CO})_3]^+$ cation, **1**, initially produce the organometallic nitroxides, **2**, and ultimately yield the diarylnitroxides, **3**, as shown in Scheme 1. In some instances, the initial unconjugated nitroxide can undergo hydrogen migration to yield a more stable second radical in which the carbon-carbon double bonds are now conjugated. Thus, the $\text{Fe}(\text{CO})_3$ -stabilized steroidal cation **4** gives the nitroxide radicals **5** and **6** successively, as in Scheme 2. These observations are in accord with the earlier reports by Cais concerning the reactions of nitroso-arenes with ferrocenyl and related cations [6,7].

In continuation of this work, we treated the cation **1** with 2-methyl-2-nitroso-propane in the expectation of observing formation of the organometallic radical **7** in which the aryl substituent in **2** had merely been replaced by a t -butyl group. However, this anticipated radical is only a minor, short-lived product and in many cases is not detectable at all. The major products **8**, **9** and **10** were characterized by their ESR spectra. Scheme 3 depicts the experimental and simulated ESR spectra of t -butyl(phenyl)nitroxide, **8**, ($g = 2.005_8$) which exhibits the usual triplet ($a_N = 13.1$ G) as well as smaller hyperfine couplings to the *ortho* (1.7 G), *meta* (0.85 G) and



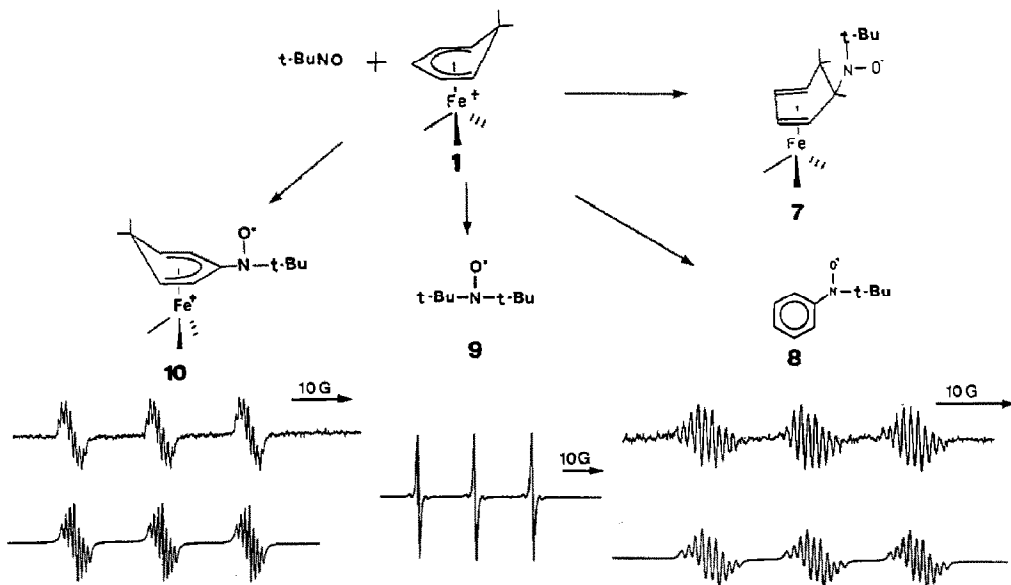
Scheme 1. The reaction of **1** with nitrosoarenes.



Scheme 2. The rearrangement of a steroidal nitroxide.

para (1.7 G) hydrogens of the phenyl ring. The simulation and comparison with the literature data [8–13] confirm the assignment of the structure of **8**. Likewise, the bis(*t*-butyl)nitroxide radical **9** has been prepared by many synthetic procedures and its ESR parameters are well known [14–16]. The structure of **10** is less trivial to establish. The radical is clearly a nitroxide ($g = 2.006_8$; $a_N = 15.3$ G) which also shows hyperfine interactions to two *ortho* (1.44 G) and two *meta* (0.72 G) protons. This leads one to assign **10** as a (cyclohexadienyl)-nitroxide but, in order to maintain its overall radical character, the cyclohexadienyl moiety must have an even π -electron count; these criteria are all satisfied by structure **10** in which the cyclohexadienyl cation is stabilized by complexation to an $\text{Fe}(\text{CO})_3$ fragment. In fact, as shown in Scheme 4, the formation of **10** can be rationalized in a straightforward manner merely by invoking hydrogen migration in the initially formed radical **7**.

Nevertheless, the most striking feature of the experiments is the oscillatory behaviour of **9**. Typically, as shown in Fig. 1, when 3.0×10^{-2} mmol of the cation **1** and a 24-fold excess of 2-methyl-2-nitrosopropane were allowed to react in dichloromethane, the (*t*-Bu)₂N–O· radical, **9**, appears for the first time 10 minutes after



Scheme 3. The ESR spectra of the products arising from the reaction of **1** with *t*-BuNO.

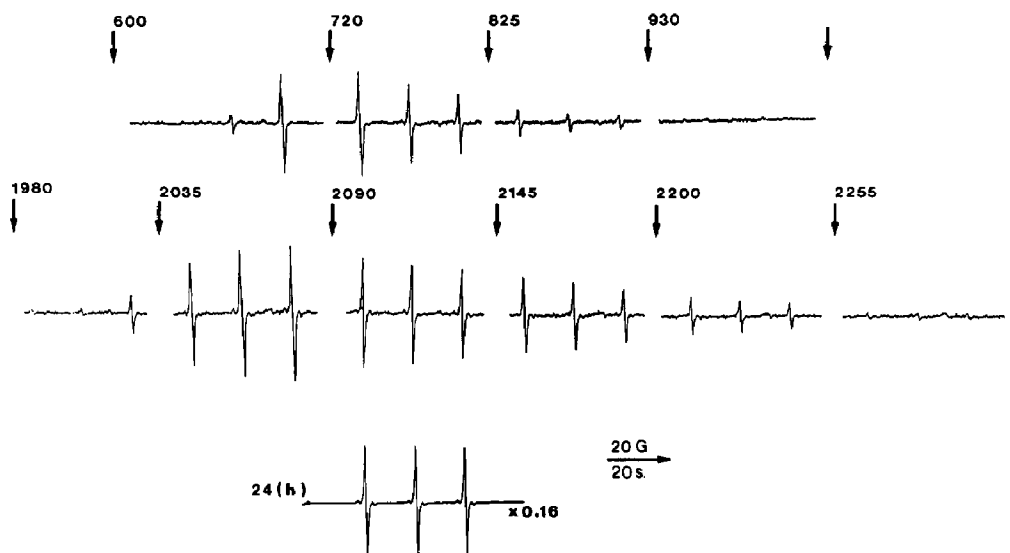


Fig. 1. The time-dependent ESR spectra observed when 3×10^{-2} mmol of **1** react with a 24-fold excess of *t*-BuNO. The initial time values are quoted in seconds from the start of the reaction.

mixing the reactants and then disappears within 4 minutes. After a silent period of 17 minutes, **9** reappears and disappears over approximately 5 minutes. The time-scale of the waxing and waning of the peak intensity of **9** is clearly shown in Fig. 1. Thus, at a scan rate of 1 gauss per second, the components of the triplet (which should of course have equal intensity) are manifestly changing.

In contrast, Fig. 2 shows the result of mixing **1** (1.6×10^{-2} mmol) with a 15-fold excess of *t*-BuNO in acetonitrile which exhibits slowly oscillating behaviour for **9**, while **10** appears only after 6 hours. In this particular case, $(t\text{-Bu})_2\text{N-O}\cdot$ appears and disappears within the first 30 minutes; this radical subsequently reappears, disappears again after ≈ 6 hours and finally reappears after 20 hrs.

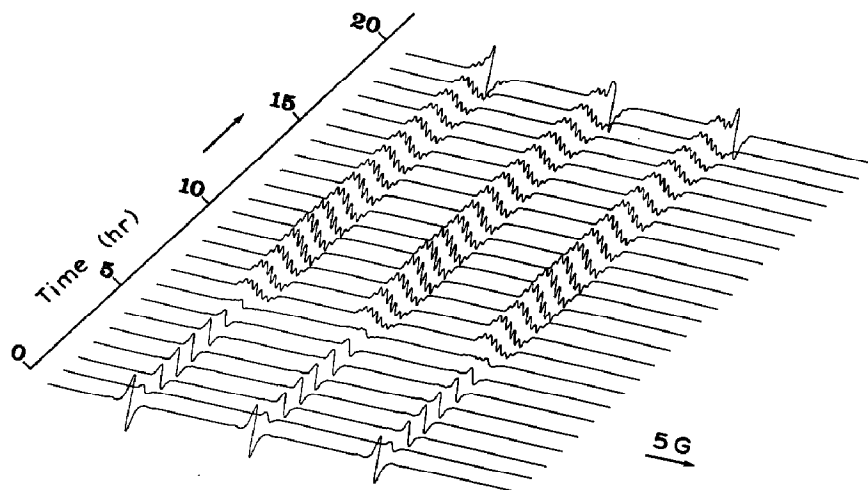


Fig. 2. ESR spectra for the reaction of 1.6×10^{-2} mmol of **1** with a 15-fold excess of *t*-BuNO.

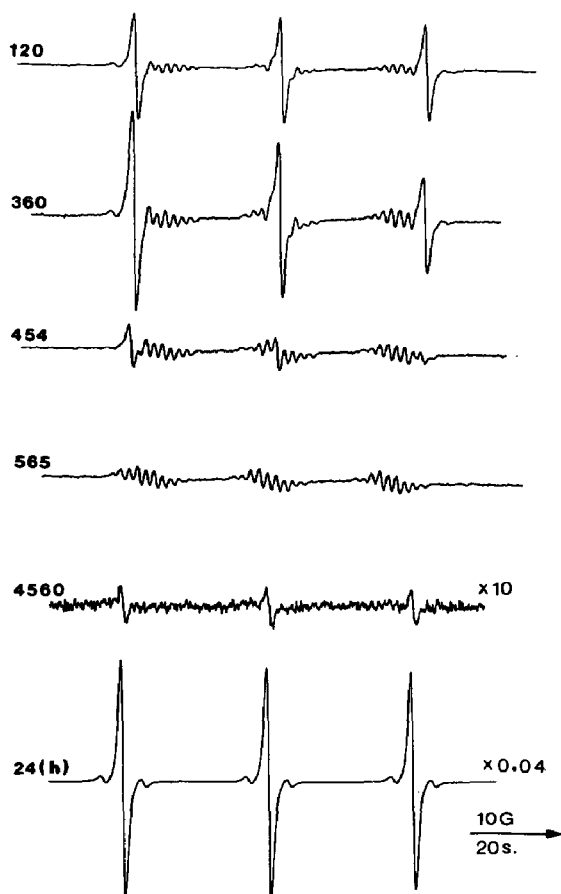


Fig. 3. ESR spectra arising from the reaction of 2×10^{-2} mmol of **1** and a 3.5-fold excess of $t\text{-BuNO}$. The initial time values are quoted in seconds from the start of the reaction.

Another example appears as Fig. 3 which shows the spectra resulting when 2.0×10^{-2} mmol of **1** and a $3\frac{1}{2}$ -fold excess of the nitroso compound are mixed in CH_2Cl_2 . Within 2 minutes one sees both **8** and **9**. After ≈ 8 minutes, the $(t\text{-Bu})_2\text{N-O}\cdot$ has disappeared leaving only $t\text{-butyl(phenyl)nitroxide}$, **8**. After 75 minutes only a very weak $(t\text{-Bu})_2\text{N-O}\cdot$ signal is detectable but the next day the triplet attributable to **9** is once again very strong.

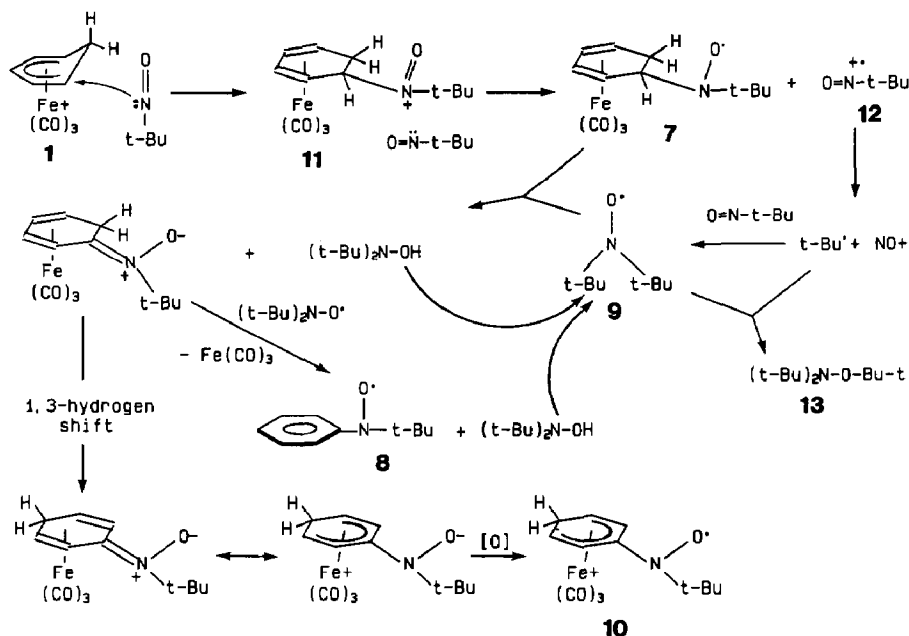
To summarize a large number of experiments, we note that oscillations are observed in acetonitrile or dichloromethane solvent but not in toluene. The radical products observed depend to some extent on the relative concentrations of the reactants. When the 2-methyl-2-nitrosopropane is present in greater than 20-fold excess, the reaction at room temperature in dichloromethane as solvent gives only the $(t\text{-Bu})_2\text{N-O}\cdot$ radical. If the concentration of $t\text{-BuNO}$ is only in the range of 3–15 times that of the organometallic cation **1** then the radicals **8** and **10** can also be observed. The delay time before the onset of the $(t\text{-Bu})_2\text{N-O}\cdot$ signal varies from zero to 40 minutes; oscillations are not observed below -20°C . The time from appearance to disappearance of **9** ranges from 4 minutes to 10 hours, while the ESR silent period between oscillations ranges from 15 minutes to one hour. Finally, it appears that high concentrations of reactants and a large excess of $t\text{-BuNO}$ lead to

more rapid oscillations. In all cases, the period of the oscillations lengthens with time and the final persistent spectrum is that of bis(*t*-butyl)nitroxide radical **9**. We have been unable to observe oscillatory behaviour using spectroscopic techniques other than ESR, e.g., UV-Vis spectroscopy nor in the NMR regime (no evidence of CIDNP). This is perhaps not surprising since the concentrations of radical species are likely to be small compared to those of diamagnetic species. Visually during the course of the reaction there is a steady change of colour from bluish-green to yellowish-green. It was observed that during the course of the ESR experiment there was some evolution of gas and the possibility was considered that the oscillatory behaviour could be an artifact brought about by removal of solution from the ESR cavity by the gas bubbles produced; however, this was shown not to be the case. The reaction was also run on a vacuum line to allow collection of the gas evolved. The major component proved to be carbon monoxide with smaller amounts of carbon dioxide (which appeared quite intense due to the higher extinction coefficient) and also methylene chloride (the solvent used). The rotational structure observed in the gas phase IR spectra allowed unambiguous identification of these species.

There are several conditions necessary for the observation of chemical oscillations. There has to be some positive feedback mechanism such that production of the oscillating species becomes more rapid as the reaction proceeds. There also has to be some reaction removing the oscillating species, which is therefore usually an intermediate rather than a final product. The following scheme fulfills these conditions.

Scheme 4 depicts a possible (speculative) mechanism to account for the observed radical products. In particular, we emphasize that the $(t\text{-Bu})_2\text{N-O}\cdot$ radical is produced and destroyed in separate steps, as required for an oscillatory mechanism. It is proposed that initial nucleophilic attack by a molecule of *t*-BuNO on the cation **1** leads to an oxo-ammonium cation **11**. (We note that an analogous cation has been observed in the reaction of $(t\text{-Bu})_2\text{N-O}\cdot$ with SbCl_5 [17]; upon warming, the oxo-ammonium cation $[(t\text{-Bu})_2\text{N=O}]^+$ decomposes to yield isobutene, NO^+ $[\text{SbCl}_6]^-$ and HCl.) We then suggest that **11** can suffer one-electron reduction by *t*-BuNO thus forming the nitroxide radical **7** and the $[\text{t-BuNO}]^{\ddagger}$ radical cation, **12**, which can fragment to give the nitrosonium ion and a *t*-butyl radical. This latter radical is well known to combine with *t*-BuNO to produce the stable $(t\text{-Bu})_2\text{N-O}\cdot$ radical, **9** [18]. It has been pointed out previously [18] that in the presence of excess *t*-butyl radicals **9** reacts to produce tri-*t*-butylhydroxylamine, **13** $(t\text{-Bu})_2\text{NO-Bu}$; such an ESR-silent product is obviously a possibility here. Since one of the products is *t*-butyl(phenyl)nitroxide, **8**, clearly it is necessary to dehydrogenate the cyclohexadienyl ring in **7**; such a process can be brought about by successive hydrogen abstractions by **8** to give the corresponding hydroxylamine, i.e., $(t\text{-Bu})_2\text{N-OH}$. We noted previously that the oscillating species is normally an intermediate rather than (as in this case) a final product. However, the reactions described here all use excess nitroso compound so the $(t\text{-Bu})_2\text{N-O}\cdot$ radical, **9**, remains after the other reagent has been completely consumed. Under these conditions, the criteria for an oscillatory system can still be satisfied.

We further propose that the radical cation **10** might arise via the 1,3-hydrogen shift process depicted in Scheme 4. Such 1,3-shifts are formally symmetry-forbidden but in this case there exists the possibility of the migration occurring via a metal hydride intermediate; we cannot rule out the possible intervention of catalytic traces



Scheme 4. A speculative mechanism for the reaction of **1** with *t*-BuNO.

of acid. Moreover, we have previously reported that nitroso-arenes can attack the central carbon of a complexed cyclohexadienyl cation [5] thus rendering unnecessary the hydrogen migration process; that is, **10** could arise directly from **1**.

The serendipitous observation of this novel oscillating system sent us searching for literature precedents. While we found much elegant experimental and theoretical work on a variety of reaction types, we were unable to find any close analogues to this particular chemical oscillator. However, we did discover that some years ago Turcsanyi [19] had proposed that a nitroxide/hydroxylamine system could in principle give rise to oscillatory behaviour under appropriate conditions. We have repeated Turcsanyi's calculations using a kinetics program written for this purpose [20] and have confirmed his results. A crucial component of any proposal to account for oscillatory behaviour is the existence of a feed-back mechanism by which a previous intermediate product can be regenerated. In this case, the important factor would appear to be the recycling of $(t\text{-Bu})_2\text{N-O}\cdot$ by oxidation of the $(t\text{-Bu})_2\text{N-OH}$, entirely analogous to the regeneration of the nitroxide intermediate in Turcsanyi's mechanistic scheme. The hydroxylamine $(t\text{-Bu})_2\text{N-OH}$, like many such species, is very readily converted to the corresponding nitroxide radical. A suitable candidate to effect this oxidation is the cationic starting material **1**.

A referee has raised the interesting point that these observations may not be of the conventional oscillatory type but instead may best be characterized as "oligo-oscillatory" or "undershoot-overshoot kinetics" [21,22]. In oligo-oscillation, different component processes are responsible for each extremum, while in true oscillation (no matter how strongly damped) the chemistry is the same in each cycle. At present, computer simulation of this fascinating system is under investigation and we therefore prefer not to speculate further but merely report our observations.

In closing, it is of interest to note that the central feature of Turcsanyi's reaction scheme is that a molecule exists in three oxidation states, separated by one-electron

transfers. It is the concentration of the middle oxidation state which oscillates, with the feedback mechanism being provided by oxidation or reduction reactions of the outer oxidation states. In the present case the middle oxidation state is represented by a nitroxide radical and the outer oxidation states by nitroso compounds and hydroxylamines. It is unlikely that this particular combination has great biological significance but carbon analogues can be readily visualized.

Experimental

ESR spectra were recorded on a Bruker ER 100D instrument operating at X-band frequency with 100 KHz modulation. The spectrometer was equipped with an ASPECT 2000 computer which was also used for spectral simulations. (η^5 -Cyclohexadienyl)tricarbonyliron(I) tetrafluoroborate was prepared as previously described [5]. 2-Methyl-2-nitrosopropane was purchased from Aldrich and was used without further purification. The ESR samples were prepared on a vacuum line. The two reactants were degassed three times separately before mixing in an ESR tube which was then sealed. The reaction mixture was kept in liquid nitrogen prior to the recording of the ESR spectra.

Acknowledgments

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