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The decay kinetics of spin adducts formed by nitrosodurene with pentacarbonylrhenium(0) radical

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Abstract

The decay of the anilino and nitroxide radicals that form by the addition of nitrosodurene to pentacarbonylrhenium(0) radical was studied by EPR spectroscopy. The anilino radical decays by first order kinetics with $\Delta H^{\neq}$ 20.5 kJ/mole and $\Delta S^{\neq}$ -196 J/mole K. The nitroxide radical decay kinetics are second order with $\Delta H^{\neq}$ 3.92 kJ/mole and $\Delta S^{\neq}$ -186 J/mole K. The isomerization of the anilino to the nitroxide form was not observed in the limited temperature range in which the anilino could be detected.

Introduction

Spin trapping techniques [1] have been widely applied in organic chemistry [2–7], biochemistry [8,9] and inorganic chemistry [10–15]. The spin trapping agent reacts with a reactive radical to form a more stable spin adduct that can be studied by various spectroscopic techniques, especially EPR, to determine the nature of the trapped radical. Thus, a radical reaction pathway and structure of radicals can be ascertained. To determine the radical structure as completely as possible, it is desirable to have a stable spin adduct. We appraoched this problem by studying the decay kinetics of the spin adducts of the $^{\cdot}Re(CO)_5$ radical.

Nitroso compounds are good trapping agents and give rise to nitroxide radicals and/or anilino radicals. However, the thermal stability and photostability of the nitroso compounds fall into a wide range [3]. Both nitrosobenzene and t-nitrosobutane decompose thermally or photochemically to generate diphenyl nitroxide and di-t-butylnitroxide radicals [15]. The formation of these nitroxide radicals may affect the reliability of the kinetic measurements owing to spectral interference and the accuracy to which the trapping agent concentration was determined. In contrast, nitrosodurene in dichloromethane produces no EPR-detectable signals either thermally or photochemically. We wish to report the results of our experiment on kinetics and the mechanism of the decay of the spin adduct formed by nitrosodurene with the $^{\cdot}Re(CO)_5$ radical.

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Experimental

Nitrosodurene was prepared by the reaction of ethyl nitrite with acetoxymercuridurene [8] which had been synthesized by mercuration of durene with mercury acetate [16].

EPR spectra and kinetic data were recorded on a Bruker 200D-SRC X-band spectrometer. It was equipped with an NMR gaussmeter (EM035), a microwave frequency counter (Bruker Model 371), a Bruker ER 4111-VT variable temperature unit and an Aspect 2000 computer. All measurements were carried out in a dual cavity. A standard DPPH (diphenylpicrylhydrazyl) sample, which has a known number of spins from comparison with several standard $MnCl_2$ solutions, was introduced through the second sample port. The DPPH standard served both as a g-value reference and as a reference for radical concentration. All spin counting measurements were carried out by comparing the heights of the double integrals of the sample and the standard DPPH EPR spectra obtained from the dual cavity with identical spectrometer settings.

Sample preparation for EPR study

The required amounts of nitrosodurene (ArNO) and $Re_2(CO)_{10}$ were introduced into a vacuum line-adaptable glass vessel, and dichloromethane solvent ($\simeq 10$ ml) was vacuum-distilled in. Four different sample concentrations used for each set: [ArNO] 2.37×10^{-2} M, $[Re_2(CO)_{10}]$ 6.04×10^{-3} M; [ArNO] 3.03×10^{-2} M, $[Re_2(CO)_{10}]$ 5.98×10^{-3} M; [ArNO] 4.76×10^{-2} M, $[Re_2(CO)_{10}]$ 5.96×10^{-3} M; [ArNO] 6.53×10^{-2} M, $[Re_2(CO)_{10}]$ 5.98×10^{-3} M.

A 4 mm-quartz tube sidearm was attached to the glass vessel to facilitate the EPR measurements. A small portion of the desired solution was transferred to the sidearm and inserted into the cavity. After temperature equilibration, the sample was irradiated with a 180-W medium pressure mercury lamp until a spectrum ($5 \simeq 6$ min) with reasonable S/N ratio was obtained. The magnetic field was then set to the peak of an EPR line, the mercury lamp was switched off and the decay of the EPR signal was then followed at the fixed magnetic field. Repetition of the UV irradiation produced an identical decay curve. A fresh sample was reintroduced into the EPR tube for similar measurements at other temperatures.

Results and discussion

The photochemical reaction in the EPR cavity between $Re_2(CO)_{10}$ and nitrosodurene gave a reaction mixture which showed a complicated EPR spectrum at temperatures below 273 K (Fig. 1a). At room temperature or higher a clean 18 line spectrum is observed. The spectral parameters (listed in Table 1) indicate that the clean 18 line spectrum can be attributed to a nitroxide radical that formed between $^{\cdot}Re(CO)_5$ and nitrosodurene, as first reported by Hudson et al. [12]. After subtracting the nitroxide radical spectrum from the observed low-temperature spectrum, another 18-line spectrum can clearly be seen, as indicated in the simulated stick diagram of Fig. 1b. The EPR parameters, as collected in Table 1, are close to those of the nitroxide radical. Since there are only two coordination sites in nitrosodurene, in addition to the *N*-coordinated nitroxide radical, there is an *O*-coordinated anilino radical, which is thought to be responsible for the second 18-line spectrum. It has

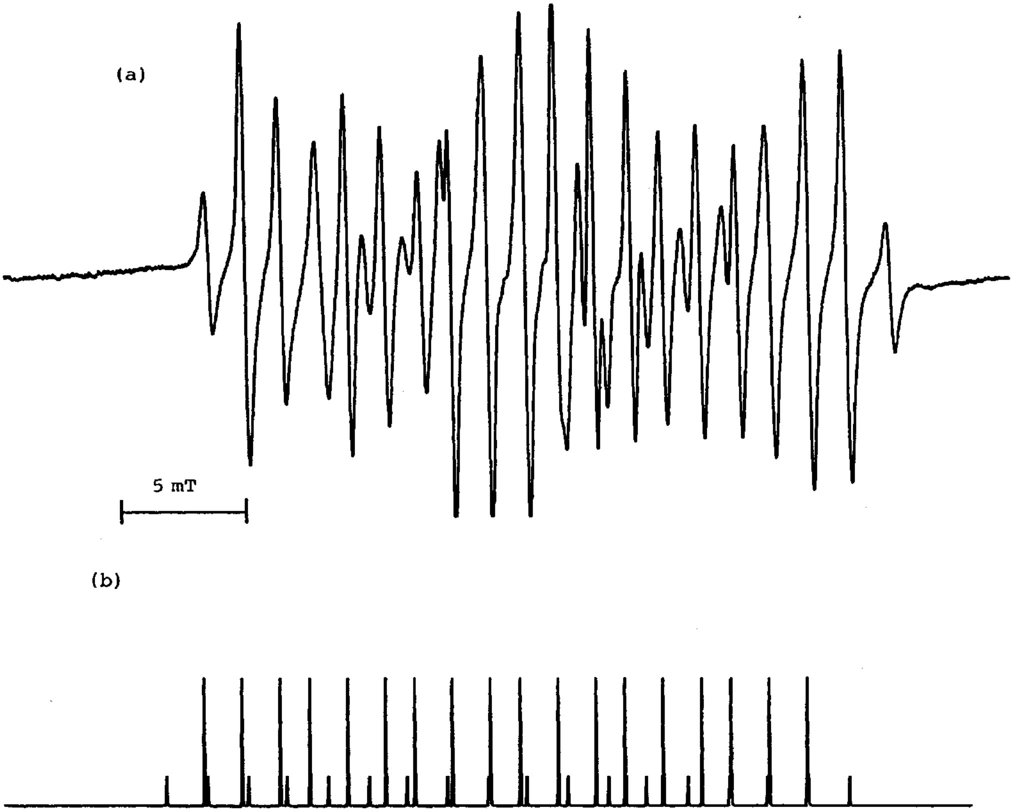


Fig. 1. (a) The EPR spectrum of a CH_2Cl_2 solution of $Re_2(CO)_{10}$ and nitrosodurene under continuous irradiation from a mercury lamp at 230 K. (b) The simulated stick spectrum. High intensity 18-line spectrum is attributed to $Ar{-}N(O^{\bullet}){-}Re(CO)_5$.

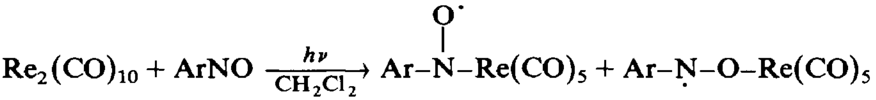
been reported that the A_N of anilino is lower than that of nitroxide for spin-trapped organic radicals [17] and $^{\bullet}Mn(CO)_5$ [14]. Clearly, this rule cannot be applied here, probably because of the presence of the third row transition element Re. But the similarity of the hyperfine coupling constants indicates that the two radicals observed at low temperature are most likely to be the nitroxide and anilino. The nitroxide and anilino radicals can be distinguished on the basis of their thermal properties. In studying the trapping of $^{\bullet}Mn(CO)_5$ with 2,4,6-tri-t-butylnitrosobenzene [14], it has been established that anilino is a kinetic product which can exist only at low temperature, and that nitroxide is a thermodynamic product. Our assumption that the radical present at temperatures below 273 K is anilino is consistent with the reported thermal behavior. Because 2,4,6-tri-t-butylnitrosoben-

Table 1

The EPR parameters of the radicals $^{\bullet}Re(CO)_5$ spin-trapped by nitrosodurene at 230 K.

Radical	g value	A_{Re} (mT)	A_N (mT)
Nitroxide	2.0085	4.068	1.455
Anilino	2.0078	4.660	1.580

zene tends to form an anilino spin adduct, a study of the spin adduct of $^{\bullet}Re(CO)_5$ with 2,4,6-tri-t-butylnitrosobenzene may help to confirm further the assignments of the nitroxide and anilino radicals. However, this attempt failed because only one type of radical was observed between 183-293 K [14]. Thus, to the best of our knowledge, the photochemical reaction between $Re_2(CO)_{10}$ and nitrosodurene can be summarized in eq. 1, where Ar represents 2,3,5,6-tetramethylphenyl group.



$$\mathrm{Re_2(CO)_{10} + ArNO \xrightarrow[CH_2Cl_2]{h\nu} Ar{-}\overset{\overset{\textstyle O^{\bullet}}{|}}{N}{-}Re(CO)_5 + Ar{-}\underset{\bullet}{N}{-}O{-}Re(CO)_5} \qquad (1)$$

All EPR parameters are independent of temperature, except for A_{Re} of the nitroxide spin adduct which is dependent on temperature, and amounts to -3.4×10^{-3} mT/K.

After the irradiating lamp had been turned off, the EPR signals decayed rapidly. From the non-overlapping spectral lines, it was possible to monitor separately the decay processes of the anilino and the nitroxide spin adducts. The lowest field line was chosen to monitor the decay kinetics of the anilino radical. After the magnetic field was adjusted to the desired EPR peak position, the irradiating lamp was switched off to allow all the EPR signals to decay completely. Then photolysis was reinitiated for $\simeq$ 4–5 min to build up the anilino radical concentration. The decay of the anilino signal was monitored immediately after the lamp was switched off. The above procedure could be repeated several times without any changes in signal strength or decay kinetics. A typical decay curve is shown in Fig. 2. It can be analyzed according to first order kinetics as shown in the insert in Fig. 2. The rate constants are shown in Fig. 3. It is obvious that the decay rate constants are independent of the concentration of nitrosodurene. The mechanism probably involves a simple unimolecular decomposition. The activation parameters are $\Delta H^{\neq}$ 20.5 ± 2.3 kJ/mole and $\Delta S^{\neq}$ -196 ± 144 J/mole K. The large standard deviation in $\Delta S^{\neq}$ stems from the rather small temperature range in which the signal can be observed. It is unusual to find a unimolecular decomposition process that has such a large negative $\Delta S^{\neq}$. We repeated the experiment several times to eliminate coincidence, but obtained the same $\Delta S^{\neq}$. The solvent must somehow be involved in the transition state. However, an attempt to study solvent effect was prevented by the poor solubility of nitrosodurene in most aprotic organic solvents.

Nitroxide decay was determined by monitoring the intensity of the fifth line in the low field of its spectrum. A typical decay curve is shown in Fig. 4. After the fast initial decay, much slower signal abatement is observed, which points to non-exponential kinetics. Indeed, a second order analysis yields a perfect fit, as shown in Fig. 4. To obtain the second order rate constant, careful spin counting was performed to determine the actual nitroxide radical concentration. The resulting rate constants are shown in Fig. 5. It is obvious that the second order rate constant is independent of the concentration of nitrosodurene, so that the mechanism of nitroxide-radical decay is consistent with a simple second order reaction. The activation parameters were found to be $\Delta H^{\neq}$ 3.92 ± 0.10 kJ/mole, $\Delta S^{\neq}$ -186 ± 6 J/mole K. The activation entropy is a rather large negative value compared with most of the other associative mechanisms. It is noteworthy that the large $\Delta S^{\neq}$ is quite close to that for anilino decay.

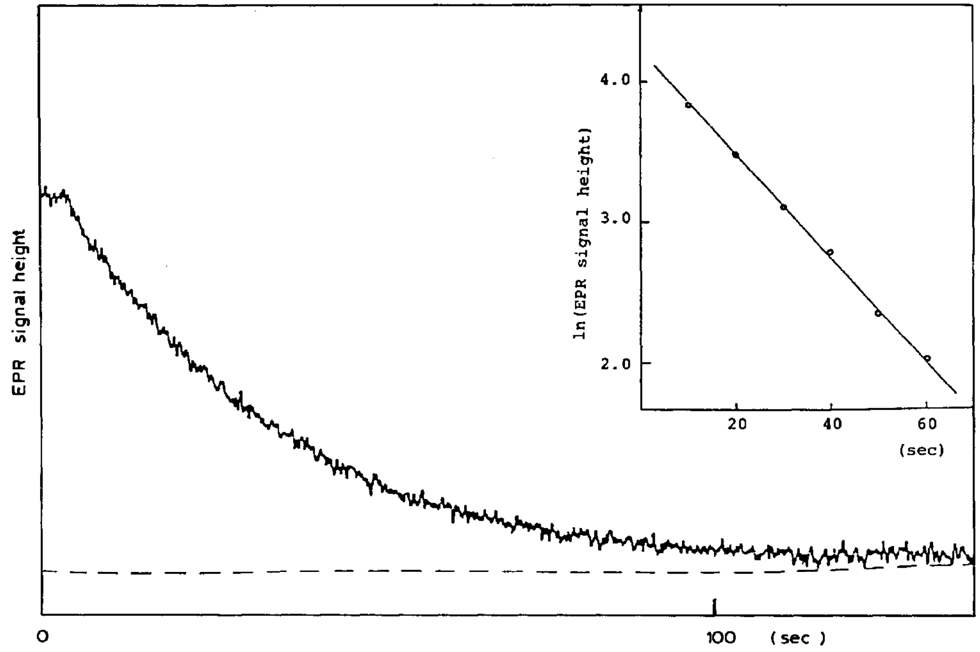


Fig. 2. The EPR signals from the decay of anilino (Ar–N$^\cdot$–O–Re(CO)$_5$) at 273 K. The insert depicts a first order analysis curve.

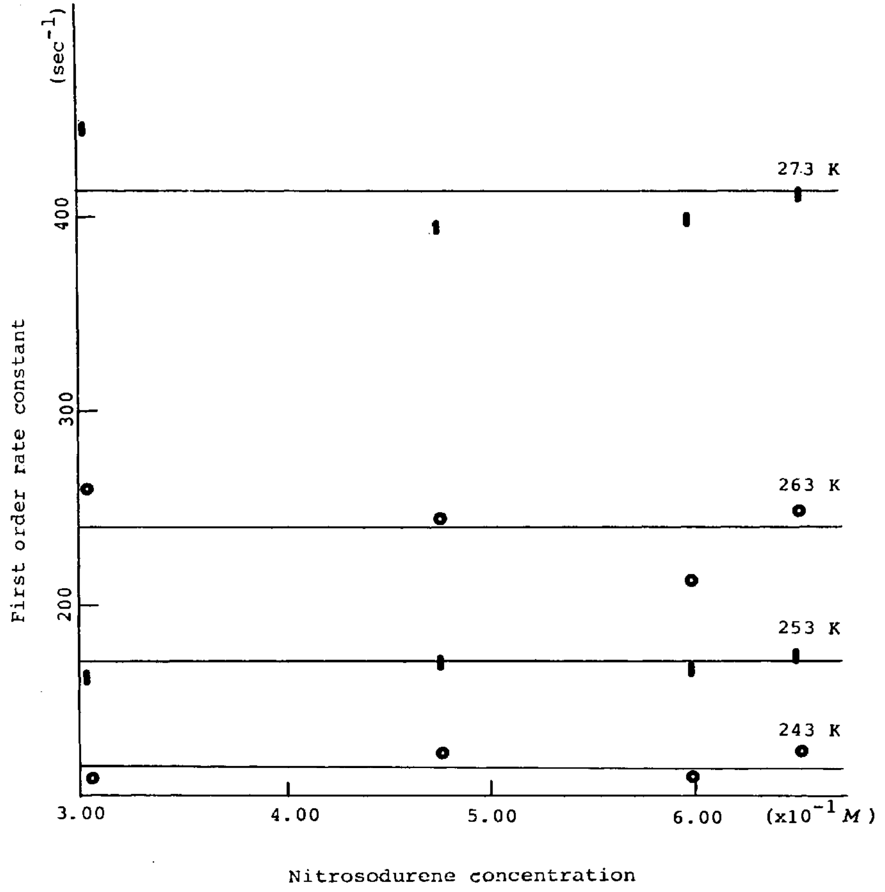


Fig. 3. The first order rate of decay of the anilino (Ar–N$^\cdot$–O–Re(CO)$_5$) radical as a function of concentration of nitrosodurene.

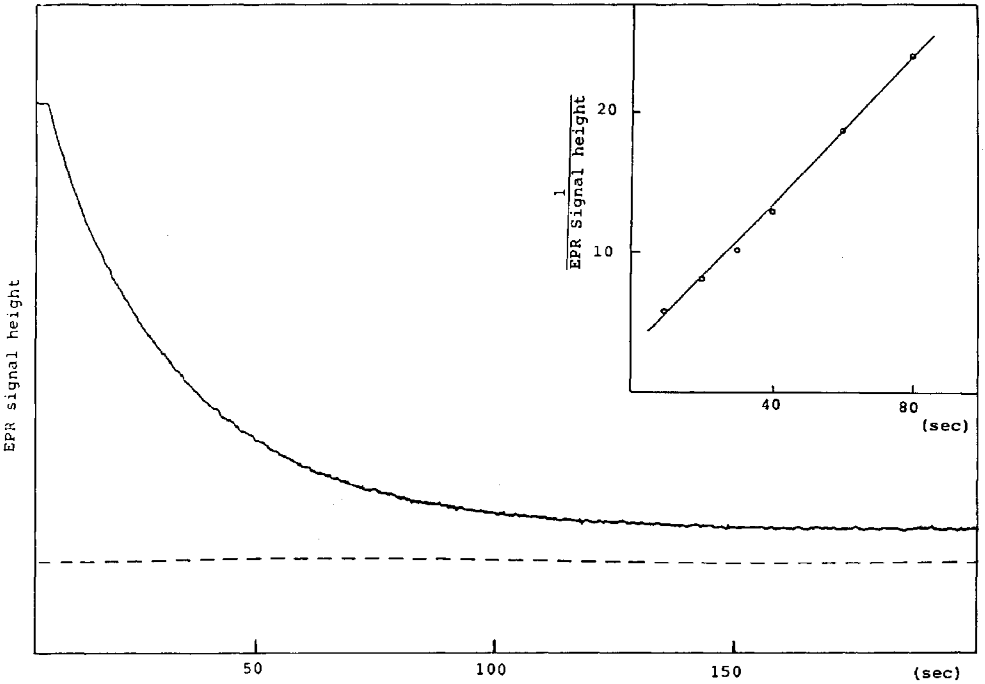


Fig. 4. The EPR signals from the decay of nitroxide (Ar–N(O$^{\cdot}$)–Re(CO)$_5$) at 313 K. The insert depicts a second order analysis curve.

Repeated irradiations and complete decay cycles were carried out at room temperature. Immediately after single irradiation, the spin counting data indicated that 6% of $Re_2(CO)_{10}$ had formed nitroxide radical. The total amount of nitroxide generated in a single irradiation cycle was even higher because of continuous decay during irradiation. After 15 cycles, the nitroxide build-up and decay were found to be identical to those of the initial stage. At lower temperature where an appreciable amount of anilino radical was present, repeated irradiations and decay experiments also gave the same results. Thus, it is obvious that both the nitroxide and the anilino decay back into the starting material.

On the basis of all the experimental data, the mechanism of anilino decay is as depicted in Scheme 1. The rate at which the radical recombinates (k_2) is diffusion-controlled [18,19], and is much larger than k_1 [4,6]. Furthermore, the equilibrium of ArNO has no effect on the decay. Hence, the measured first order rate of decay of the anilino radical is the unimolecular rate constant k_1.

The mechanism of nitroxide formation is depicted in Scheme 2. Since $\Delta H^{\neq}$ is small, the Re–Re and/or N–N bond must be partially formed in the transition state, resulting in a rapid transformation into $Re_2(CO)_{10}$ and nitrosodurene. No experimental data were available to distinguish between the k_4 and k_5 pathways.

We have reinvestigated the spin addcut formed between 2,4,6-tri-t-butylnitrosobenzene in a temperature range from 210 to 310 K. At 230 K, its EPR parameters are $g = 2.0072$, A_{Re} 1.445 mT, A_N 1.278 mT and A_{2H} 11.51 mT, which are close to the values reported previously, A_{Re} and A_N show only a slight dependence temperature with coefficients of -1.0×10^{-3} mT/K and -0.60×10^{-3} mT/K respectively. This spin adduct decays by second order kinetics. Thus, the only spin

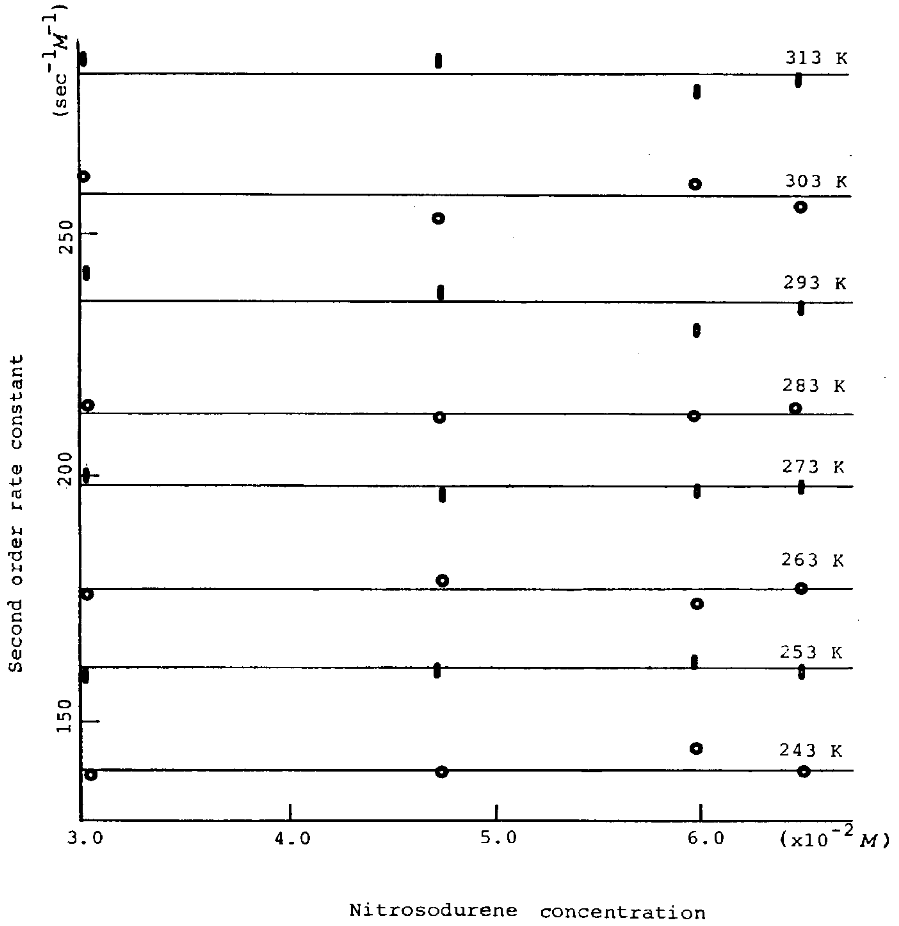


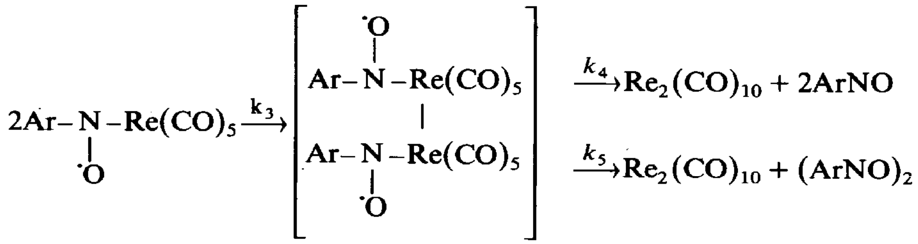
Fig. 5. The second order rate of decay of the nitroxide (Ar–N(O$^{\bullet}$)–Re(CO)$_5$) radical as a function of the concentration of nitrosodurene.

$$\mathrm{Ar\dot{N}O{-}Re(CO)_5} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{Ar{-}NO} + {}^{\bullet}\mathrm{Re(CO)_5} \tag{2}$$

$$2\,{}^{\bullet}\mathrm{Re(CO)_5} \xrightarrow{k_2} \mathrm{Re_2(CO)_{10}} \tag{3}$$

$$2\mathrm{ArNO} \overset{K}{\rightleftarrows} (\mathrm{ArNO})_2 \tag{4}$$

Scheme 1



$$2\,\mathrm{Ar{-}}\underset{{}^{\bullet}\mathrm{O}}{\mathrm{N}}\mathrm{{-}Re(CO)_5} \xrightarrow{k_3} \left[\begin{array}{c} \mathrm{Ar{-}}\overset{{}^{\bullet}\mathrm{O}}{\mathrm{N}}\mathrm{{-}Re(CO)_5} \\ | \\ \mathrm{Ar{-}}\underset{{}^{\bullet}\mathrm{O}}{\mathrm{N}}\mathrm{{-}Re(CO)_5} \end{array}\right] \begin{array}{l} \xrightarrow{k_4} \mathrm{Re_2(CO)_{10}} + 2\mathrm{ArNO} \\ \xrightarrow{k_5} \mathrm{Re_2(CO)_{10}} + (\mathrm{ArNO})_2 \end{array}$$

Scheme 2

adduct of $^{\cdot}Re(CO)_5$ with 2,4,6-tri-t-butylnitrosobenzene and the $Ar-N(O^{\cdot})-Re(CO)_5$ radical show similar behaviour, despite the fact that 2,4,6-tri-t-butylnitrosobenzene tends to form anilino spin adducts with organic radicals [7]. The exact reason is not clear.

From the decay kinetics, it becomes clear that to generate a stable anilino radical, it is desirable to form a strong Re–O bond and simultaneously keep $\Delta S^{\neq}$ as low as possible. The design of spin traps with strong Re–O bonds requires an understanding of the nature of this chemical bond. Since there is a substantial electron transfer from $^{\cdot}Re(CO)_3PPh_3$ to DTBQ (DTBQ = 3,5-di-butylbenzoquinone) in the radical $DTBQ-{}^{\cdot}Re(CO)_3(PPh_3)$, as evidenced by its crystal structure [20] where DTBQ can best be regarded as a semiquinone, we think that charge transfer may also be significant in the nitroso spin adduct. In line with this, a spin trapping agent with a low energy π^* orbital should form a stable anilino radical. The charge transfer bonding scheme is also consistent with the explanation for the large negative $\Delta S^{\neq}$. To make a stable nitroxide radical, it is best to utilize steric influences. A bulky spin trapping agent can prevent the nitroxide spin adducts from approaching each other closely enough to cause a second order decay.

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