Reactivity of 4-R-1,2,4-triazoline-3,5-diones towards nitrone spin-traps: spectral study of the reaction with 5,5-dimethyl-pyrroline-N-oxide

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Previous studies of the reactivity of 4-R-1,3,4-triazoline-3,5-diones (R = CH$_3$, C$_6$H$_5$) have shown that, when 5,5-dimethylpyrroline-N-oxide (DMPO) is used as a spin-trap, a thermal reaction between the dione and the spin-trap occurs, leading to the same spin-adduct as by proper spin-trapping. Therefore, the reaction between two 4-R-triazolinediones (RTAD) with DMPO was investigated by combined spectral methods, including UV–Visible, FT-IR, ^{1}H and ^{13}C NMR and EPR spectroscopy. The results were rationalised in terms of a reaction sequence in which the spin-adduct is formed *via* a modified version of the Forrester–Hepburn mechanism and the rate determining step is the oxidation of the spin-adduct by RTAD, leading to the final product.

Introduction

Previous investigation of the reaction mechanism of 4-methyl-1,2,4-triazoline-3,5-dione (MTAD) with saturated ethers[1] has evidenced the presence of two paramagnetic species, the anion-radical and the urazolyl radical. At room temperature in solution only the anion-radical is persistent enough, in conditions of continuous generation, to be studied directly by EPR spectroscopy.

In order to evidence the less stable urazolyl radical, spin-trapping experiments were employed, using 5,5-dimethyl-pyrroline-N-oxide (DMPO) as a spin-trap.

It was stated that adding DMPO to a solution of MTAD in different ethereal solvents led to the rapid disappearance of the colour and to an intense EPR spectrum, characteristic of a spin-adduct with a nitrogen-centred radical. The main spectral features of the spin-adduct in the investigated solvents are similar, *i.e.* a nitrogen coupling constant in the range 1.3–1.4 mT, a proton splitting of 1.8–1.9 mT and a second nitrogen splitting of 0.27–0.28 mT.

However, although the trapping of urazolyl radicals by DMPO at room temperature was proved, the reaction between DMPO and RTAD's does not present the main features of a photochemical reaction, no irradiation being necessary for the appearance of the spin-adduct. As other mechanisms can lead to spin-adducts, implying thermal reactions of the spin-traps, we focused our attention on the mechanism of the reaction of RTAD's with DMPO.

Therefore a spectral investigation, including UV–VIS, FT-IR and NMR spectrometry in combination with EPR, was performed on the reaction of two RTAD's with DMPO in different solvents (Formula **1**).

Results and discussion

A. EPR results

A typical spectrum of the spin-adduct obtained by mixing an MTAD solution in acetonitrile with DMPO is presented in Fig. 1 and the EPR parameters of the spin-adducts obtained from both triazolinediones in different solvents are listed in Table 1.
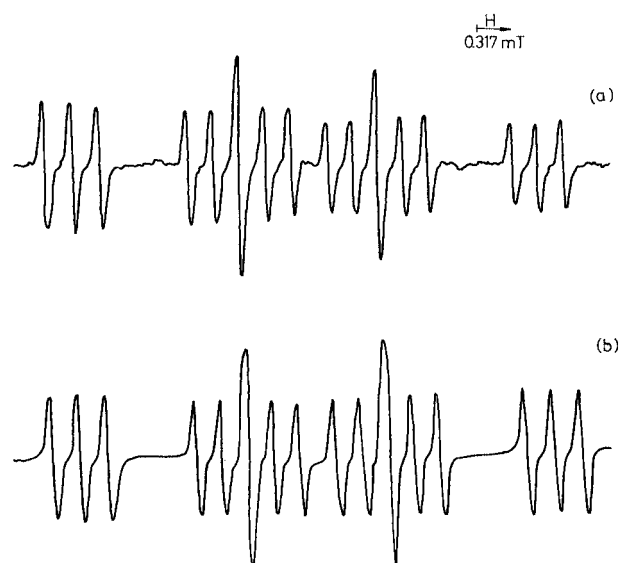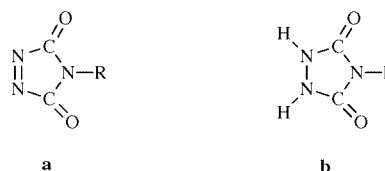

Fig. 1 The EPR spectrum of the spin-adduct of MTAD with DMPO in acetonitrile: a) experimental, b) simulated with the parameters in Table 1.

Formula **1**. Investigated compounds: **a**) R-triazolinediones (MTAD: R = CH$_3$, PTAD: R = C$_6$H$_5$) and **b**) R-urazoles (Ur–H).

These results are compatible with a spin-adduct of DMPO with a nitrogen centred radical, presumably the urazolyl radical.

In order to verify that the trapped species is the RTAD and not a transient species resulting from its decomposition, a FT-IR and NMR (^{1}H and ^{13}C) spectral analysis of the reaction

Table 1 EPR parameters of the spin-adducts of MTAD and PTAD with DMPO in different solvents

| RTAD	Solvent	g	a_N^{NO}/mT	a_H^β/mT	a_N/mT	δ/mT
MTAD	CH$_2$Cl$_2$	2.0057	1.386	1.890	0.284	0.094
	CCl$_4$	2.0056	1.295	1.770	0.255	0.092
	CH$_3$CN	2.0059	1.379	1.902	0.269	0.079
	DMSO	2.0059	1.426	1.917	0.269	0.079
	THF[a]	2.0059	1.345	1.841	0.278	0.077
	C$_2$H$_5$OC$_2$H$_5$[a]	2.0059	1.340	1.862	0.280	0.078
PTAD	CH$_2$Cl$_2$		1.435	1.965	0.281	0.094
	CCl$_4$		1.342	1.856	0.281	0.094
	CH$_3$CN	2.0059	1.377	1.878	0.250	0.078
	DMSO		1.338	1.824	0.266	0.122
	THF[a]		1.315	1.831	0.250	0.094
	C$_2$H$_5$OC$_2$H$_5$[a]		1.342	1.841	0.249	0.078

[a] In ethereal solvents (diethyl ether, tetrahydrofuran) lines of small intensity belonging to another radical species presenting the features of an aminoxyl ($a_N = 1.3$ mT) were observed. These lines could not be assigned with certitude, but as they increase in intensity if the solvent is not carefully purified, they could be due to the trapping by DMPO of superoxide radicals formed by peroxide impurities in the ether.

Table 2 ^{1}H and ^{13}C NMR (400 MHz, DMSO-d$_6$) parameters for the reaction product of the reaction of DMPO with MTAD

| ^{1}H			^{13}C	
δ (ppm)	J/Hz	Assignment	δ (ppm)	Assignment
1.32 (s)	—	2 CH$_3$	24.1	CH$_2$ (A)
2.06 (t)	7.5	CH$_2$ (A)	24.6	2 CH$_3$
2.92 (s)	—	N-CH$_3$	27.7	N-CH$_3$
3.08 (t)	7.5	CH$_2$ (B)	31.1	CH$_2$ (B)
7.60 (s)	—	N-H	70.5	C(CH$_3$)$_2$
			134.8	C=N
			149.2	C=O
			151.3	C=O

products was performed. The results are summarised in Table 2 and they confirm the structure of the reaction product as Formula **2**.
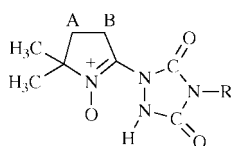
Formula **2**. Final reaction product of RTAD with DMPO.

The presence of both carbonyl groups and of the carbon atom in the N-CH$_3$ group is attested by the ^{13}C NMR spectrum, confirming the trapping of MTAD as a whole. The absence of the H$_\beta$ in the DMPO moiety is also to be noted, as shown by the signals of the A and B protons at 2.06 and 3.08 ppm, respectively, in the ^{1}H NMR spectrum.

Further confirmation of the structure of the spin-adduct was obtained starting from methylurazole oxidised by PbO$_2$. Addition of DMPO to the reaction mixture led to the same spin-adduct as in the former case. On this basis the structure **3** was assigned to the spin-adduct.
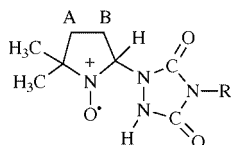
Formula **3**. The spin-adduct of RTAD with DMPO.

B. Electronic spectra

In order to get more information about the reaction leading to the spin-adduct **3** and then to the final product **2**, the reaction
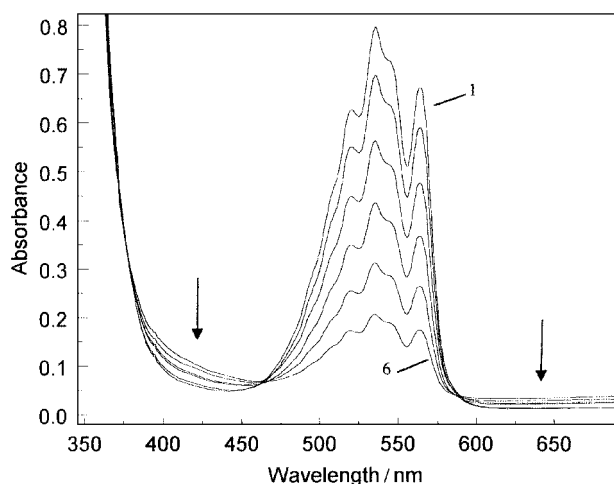
Fig. 2 Family of curves obtained when DMPO is added gradually to a MTAD solution in CH$_2$Cl$_2$ ($c_{MTAD} = 1.12 \times 10^{-2}$ M, $c_{DMPO} = 4.4 \times 10^{-4}$ M (1), 8.8×10^{-4} M (2), 1.73×10^{-3} M (3), 2.14×10^{-3} M (4), 2.54×10^{-3} M (5), 2.93×10^{-3} M (6)). Further spectra do not pass any more by the isosbestic points, all bands decrease (the new bands decreasing simultaneously with the dione band).

was followed in the visible spectra in the n–π* band of the dione. Two kinds of experiments were performed:

1) adding small amounts of a solution of DMPO to a solution of MTAD in the same solvent (CH$_2$Cl$_2$), the family of spectra in Fig. 2 was recorded; the decrease of the dione n–π* band and the appearance of two new absorption ranges of weak intensity, at 417–430 and 625–700 nm, respectively, were observed. Taking into account the literature data on the optical spectra of other aminoxyl radicals,[2] and of the radical species provided by different RTAD's,[3] these absorption ranges were tentatively assigned to the spin-adduct. Further support for this assignment is the fact that the weak absorption band in the range 625–700 nm is markedly increased when more concentrated solutions ($\sim 3 \times 10^{-2}$ M) are mixed in a 1 : 1 molar ratio (see Fig. 3).

2) mixing the two initial solutions in different molar ratios and following the time evolution of the spectrum. In Fig. 3 a family of curves registered for a mixing molar ratio of 1 : 1 is presented.

The first spectrum, registered immediately after mixing, shows, besides the n–π* band of MTAD, an intermediate species characterised by a band at 683 nm and enhanced absorption in the range 400–450 nm. Both bands decrease slowly until the complete disappearance. The spectrum registered the next day presents only an absorption band at 285 nm ($\varepsilon = 27233$ l mol^{-1} cm^{-1}) which is in agreement with the
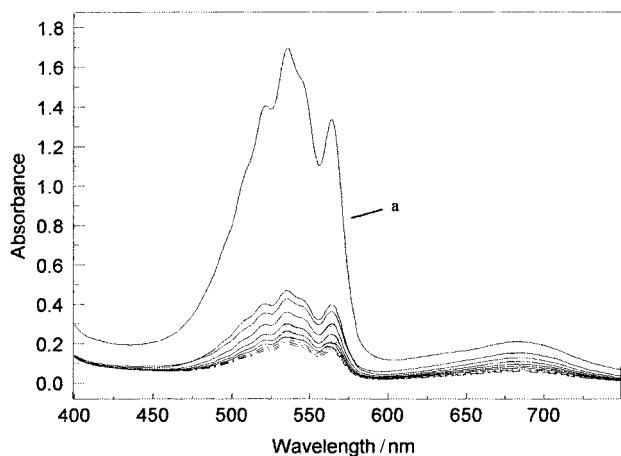
Fig. 3 Time-evolution of a 1:1 (molar ratio) mixture of MTAD and DMPO in CH_2Cl_2 ($c = 2.75 \times 10^{-2}$ M). Spectrum (a) was recorded immediately (*ca.* 40 s) after mixing. The other spectra were recorded at 1 min 28 s time intervals.

structure **2** of the final product, rather similar to a substituted urazole. This time evolution suggests very rapid formation of the intermediate species in a reaction consuming only partly the dione, followed by a less rapid evolution to the final product, consuming the remaining dione.

It was also observed that when DMPO is in excess the time evolution is too rapid to be followed by usual spectrophotometric methods.

Kinetic studies in the n–π* band of the dione were followed in two solvents, carbon tetrachloride and methylene chloride, for MTAD and in acetonitrile for PTAD, because of its lack of solubility. Starting from concentrations of MTAD greater than those of DMPO, the decrease of the dione concentration always corresponds to the quantity of DMPO, so the combination ratio is always 1:1 (a small quantity of dione is not recovered, probably due to parallel photochemical decomposition reactions, as the reaction was performed at the laboratory light exposure). The bands assigned to the spin-adduct are very weak and therefore kinetic studies in the absorption band of the intermediate could not be performed.

C. FT-IR results

The reactions of MTAD and PTAD with DMPO were also followed by FT-IR spectrometry. The spectra of DMPO–MTAD in CCl_4 and the spectrum of the 1:1 molar ratio mixture were registered in the first moments and about 2 h after mixing. The main modifications as against the reactants are observed in the range 1500–1800 cm^{-1}. The intense band at 1586 cm^{-1}, assigned to the valence vibration C=N in the group C=N–O (imine-oxide) in DMPO, disappears in the first moments after the mixing of the two solutions; this behaviour supports the formation of the spin-adduct, where this structure is not present. In the spectrum of the final product, a band of lower intensity at 1635 cm^{-1}, assigned to the group vibration $v_{(>N-C=N-)}$ is apparent, in agreement with the structure of the final product **2**, determined by NMR spectrometry.

The modifications observed in the range of the carbonyl vibrations imply the two carbonyl stretching vibration modes, the antisymmetrical at 1781 cm^{-1} (intense) and the symmetrical at 1742 cm^{-1} (weak) in MTAD, which become 1785 cm^{-1} (weak) and 1730 cm^{-1} (intense) in the product, switching the intensities. The same switching of intensities is observed when MTAD is compared with methylurazole, or with any substitution derivative of methylurazole.[4] As the structures **2** and **3** proposed for the reaction product and the spin-adduct respectively are rather similar to substituted urazoles, this intensity switching may be considered further evidence for the formation

of the spin adduct in the first moments after mixing the reagents.

The time evolution of the spectrum in the carbonyl range frequencies in Fig. 4a allows assignment of the frequencies at 1717 and 1778 cm^{-1} to the intermediate, presumably the spin-adduct, which evolves to the reaction product, characterised by the bands at 1785 cm^{-1} (weak) and 1730 cm^{-1} (intense).

A similar behaviour was noted in the reaction of PTAD with DMPO and is reflected by the spectra in Fig. 4b. The first spectrum after mixing demonstrates a marked decrease of the dione band at 1778 cm^{-1} and the appearance of intense and broad absorption in the range 1710–1750 cm^{-1}. Further evolution implies the slower decrease of the dione band and of the band at 1745 cm^{-1}, simultaneously with the increase of the species characterised by bands at 1730 and 1786 cm^{-1}. This time evolution with isosbestic points suggests the transformation of the intermediate, with a band at 1745 cm^{-1}, into the final reaction product characterised by bands at 1786 cm^{-1} (weak) and 1730 cm^{-1} (intense), in a reaction consuming the remaining dione.

The time evolution of the IR-spectra allows the following comments regarding the kinetics of the process:

—the spin-adduct is formed rapidly after mixing the two solutions, RTAD and DMPO, in a 1:1 molar ratio;

—the time evolution observed in Fig. 4a,b is in fact the transformation of the spin-adduct into the reaction product. This means that the cleavage of the C–H$_\beta$ bond is the slow, rate-determining step of the whole process. This agrees with the statements in the visible spectra which attest the rapid diminution of the dione band in the first moments, followed by a slower diminution afterwards;

—the isosbestic points suggest the presence of only two species, the spin-adduct **3** and the final product **2**. However quantitative treatment of the data is difficult because the carbonyl bands of RTAD, spin-adducts and products are too close to each other and superimposed.

Examination of the results of the visible, FT-IR and EPR spectra shows that the reaction between RTAD's and DMPO leading to the spin-adduct does not present the features of usual spin-trapping mechanisms, at least as a major pathway.

Although it is closely related to the reaction of PTAD with pyridine *N*-oxide,[5] the structure of the final product in our case rules out the formation of betaine, at least as a principal product. Therefore we believe that this is not a 1,3-dipolar cycloaddition and in fact an intermediate with a zwitterionic character could not account for the spin-adduct observed by EPR.

Recent developments of the spin-trapping technique[6] have shown that, using nitrones as spin-traps, three mechanisms to obtain spin-adducts are possible:

1) radical addition, represented by the reaction:

$$ST + R^\bullet \longrightarrow R–ST^\bullet$$
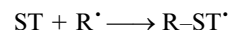
and usually called "proper spin-trapping";

2) oxidation of the spin-trap to the corresponding cation-radical, followed by the addition of a nucleophile:

$$ST + Ox \longrightarrow ST^{\bullet+} + Red$$

$$ST^{\bullet+} + R^- \longrightarrow R–ST^\bullet$$
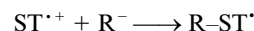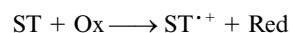
called "inverted spin-trapping". This case is frequently encountered in photochemical experiments where the excited states of different molecules act as strong oxidants;

3) addition of a nucleophile R$^-$, resulting in the formation of hydroxylamines which are readily oxidised by weak oxidants to form the spin-adduct:
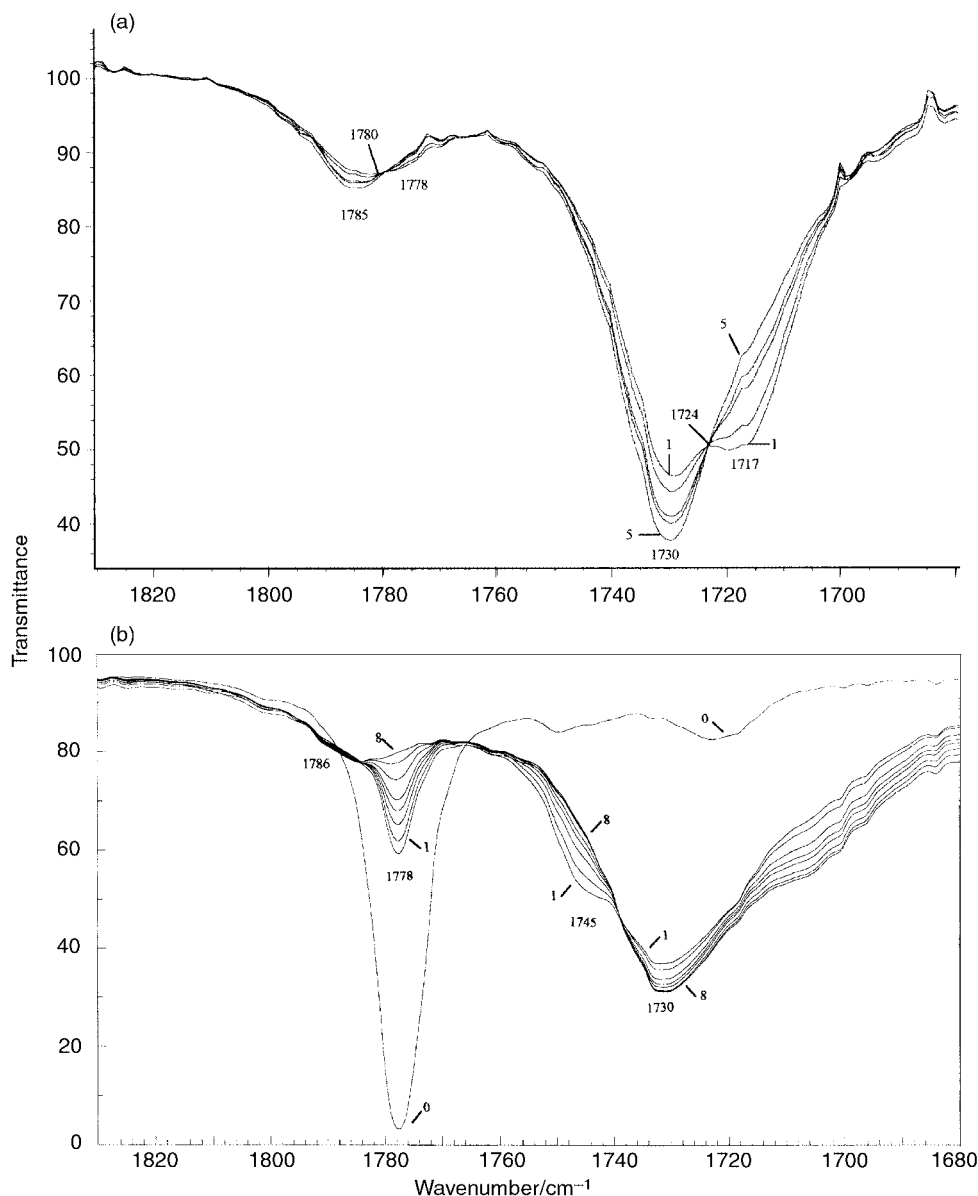
$$ST + R^- \rightleftharpoons R–ST^-$$

$$R–ST^- + Ox \longrightarrow R–ST^\bullet + Red$$
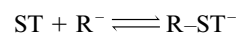
Fig. 4 Time-evolution of the FT-IR spectrum in the carbonyl range frequencies for a 1:1 molar ratio mixture: a) MTAD and DMPO in CCl$_4$, $c = 5 \times 10^{-2}$ M, spectrum (1) was recorded at *ca.* 1 min after mixing, spectrum (5) after about 2 h; b) PTAD and DMPO in ACN, $c = 5 \times 10^{-1}$ M, spectrum (1) $t = 45$ s, (2) $t = 2$ min, (3) $t = 3.36$ min, (4) $t = 6.28$ min, (5) $t = 10$ min, (6) $t = 15$ min, (7) $t = 18.85$ min, (8) $t = 23$ min.

This pathway is especially probable in alkaline media because the anion of the hydroxylamine has a much lower oxidation potential and may be oxidised even by very weak oxidants present in solution, like dissolved oxygen, for example. This mechanism was first reported by Forrester[7] and it was found to operate for amines which can give spin-adducts with DMPO spontaneously; ionic addition followed by mild oxidation appears to be the mechanism[8] and it is usually called the "Forrester–Hepburn mechanism".[9]

An alternative version of this mechanism implies the addition in the first step of an acid AH to the nitrone function, followed by oxidation of the resulting hydroxylamine by relatively weak oxidants and leading to the corresponding spin-adduct. A spontaneous thermal reaction between a spin-trap and a weak electron-acceptor to give a spin-adduct was encountered in the case of phenyl-*tert*-butylnitrone (PBN) and trichloroacetonitrile in hexane,[9] the reaction of PBN and DMPO with (C$_6$H$_5$–SO$_2$)N–F in CH$_2$Cl$_2$,[10] and also in the reaction between *N*-chlorobenzotriazole and PBN with benzotriazole as catalyst.[11] It was also stated that DMPO reacts much faster than PBN according to this type of mechanism.[11]

Examination of the experimental results in our work conditions reveals that the reaction of the RTAD's with DMPO presents the features of a spontaneous thermal reaction, rather than of a photochemical one. Consequently, the formation of the spin-adduct according to mechanism (1) implying radical addition of urazolyl radicals formed by hydrogen abstraction by the dione in its S$_1$ or T$_1$ excited state seems to be less probable, at least as a principal pathway. This would not explain either the formation of the same spin-adduct in CCl$_4$ or in poor hydrogen donor solvents like ACN.

Path (2), implying oxidation of the spin-trap by RTAD's, is also highly improbable, as the oxidation potential of DMPO is 1.9 V/NHE whereas the reduction potentials[12] of the RTAD's are in the range of (+0.31)–(+0.38) V/NHE. This renders this process endergonic by about 146.4 kJ mol^{-1} and consequently of low probability, even in low relative permittivity solvents like CCl$_4$, where the electrostatic energy of the ion-pair formed would probably compensate partly this endergonicity.[13]

Therefore, corroborating the EPR results with the spectral UV–VIS, FT-IR and NMR data, the following mechanism as a version of pathway (3), already discussed, may be proposed.

The RTAD solutions in different solvents always contain traces of urazole (urazole impurities in catalytic concen-
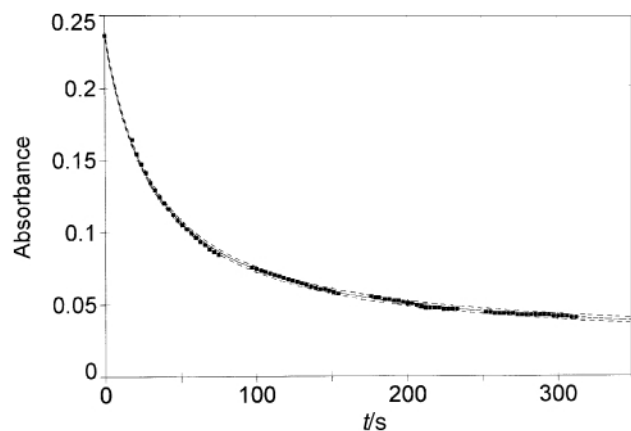
Fig. 5 The kinetic curve of the MTAD ($c_{MTAD} = 1.45 \times 10^{-3}$ M) with DMPO ($c_{DMPO} = 1.98 \times 10^{-3}$ M) reaction in CCl$_4$, followed in the n–π* band of MTAD (572 nm).

trations) or tetrazane which can decompose to give urazole and the corresponding RTAD. These urazole traces may add to DMPO to give the corresponding hydroxylamine, according to reaction (1).

$$\text{DMPO} + \text{Ur–H} \rightleftharpoons \text{DMPO(H)Ur} \qquad (1)$$

This is easily oxidisable by weak oxidants, as already pointed out in the literature (oxidation potentials in the range (+0.5)–(+0.7) V/SCE, decreasing to (−0.7) V under basic conditions.[14] As the RTAD's have reduction potentials in the range of (+0.31)–(+0.38) V/NHE, reaction (2) becomes thermally
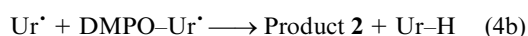
$$\text{DMPO(H)Ur} + \text{RTAD} \rightleftharpoons \text{DMPO–Ur}^{\bullet} + \text{Ur}^{\bullet} \qquad (2)$$
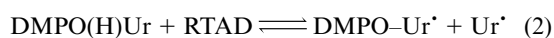
feasible, where DMPO–Ur$^{\bullet}$ stands for the corresponding spin-adduct (formula **3**) and Ur$^{\bullet}$ for the urazolyl radical.
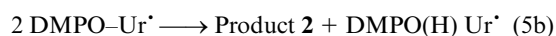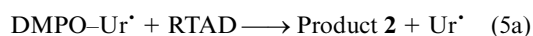
The urazolyl radical may be trapped by another molecule of DMPO [reaction (3)] or, being a good hydrogen atom abstrac-

$$\text{DMPO} + \text{Ur}^{\bullet} \rightleftharpoons \text{DMPO–Ur}^{\bullet} \qquad (3)$$

tor, can abstract a H-atom from a suitable H-donor in solution. This can be either the solvent or the spin-adduct itself (H$_\beta$). The final product is thus formed and the urazole, which can initiate a new cycle [reactions (4a), (4b)].

$$\text{Ur}^{\bullet} + \text{H–S} \longrightarrow \text{Ur–H} + \text{S}^{\bullet} \qquad (4a)$$

$$\text{Ur}^{\bullet} + \text{DMPO–Ur}^{\bullet} \longrightarrow \text{Product } \mathbf{2} + \text{Ur–H} \qquad (4b)$$

Evolution of the spin-adduct **3** to the final product **2** implies the cleavage of the C–H$_\beta$ bond, a rather slow reaction, characteristic of aminoxyls having a H in the β position. This can be done by a hydrogen-atom abstracting agent present in solution, *i.e.* RTAD, the urazolyl radical [reaction (4b)] or another molecule of spin-adduct in a dismutation reaction[2] [reaction (5b)].

$$\text{DMPO–Ur}^{\bullet} + \text{RTAD} \longrightarrow \text{Product } \mathbf{2} + \text{Ur}^{\bullet} \qquad (5a)$$

$$2\,\text{DMPO–Ur}^{\bullet} \longrightarrow \text{Product } \mathbf{2} + \text{DMPO(H) Ur}^{\bullet} \qquad (5b)$$

In our work conditions hydroxylamine was not found among the reaction products, which can be explained either by the fact that the dismutation reaction (5b) is less probable than reaction (5a), RTAD being a better H-atom abstractor, or that, once formed, it is rapidly oxidised by RTAD according to reaction (2).

The time evolution of both visible and IR spectra has revealed that the transformation of the spin-adduct **3** into the

final product **2** is a slow reaction, being the rate-determining step for the whole process. The proposed mechanism would explain this by the C–H$_\beta$ cleavage reaction (5), known to be slow.[2] It would also explain the rapid consumption of a part of RTAD [reactions (1) and (2)] and the rapid formation of the spin-adduct, followed by a slower decay of the remaining dione, according to reaction (5a), in agreement with both visible and IR spectral data. It would also account for the DMPO–RTAD combination ratio, the global reaction [eqn. (1)–(5)] corresponding to a 1:1 molar ratio not taking into account the reaction with the solvent (4a) or the dimerization reaction (5b).
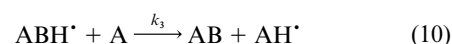
The high increase of the rate of disappearance of the dione when the concentration of DMPO is greater than that of the dione may be explained by the rapid consumption of the urazolyl radicals according to eqn. (3) (proper spin-trapping, known to be rapid), which shifts the equilibrium (2) to the right, *i.e.* to the formation of the spin-adduct **3**.

This mechanism would also explain the formation of the same spin-adduct in all solvents employed, hydrogenated or not. In solvents having H-donor capacity like CH$_2$Cl$_2$ it is expected that reaction (4a) will be as important as (4b), ensuring the formation of urazole and increasing the global reaction rate, in agreement with the experimental statement that the rate is greater in CH$_2$Cl$_2$ than in CCl$_4$.

Other reactions which can account for minor reaction pathways are not excluded; *i.e.* the loss of a small quantity of dione by photochemical decomposition to N$_2$, CO and R-isocyanate is possible, as the laboratory light exposure allows the excitation of the dione to the S$_1$ state. Acid dissociation of the urazolyl radicals leading to the anion-radicals is also possible, taking into account the pK_a values (9 and 11 for MTAD and PTAD in DMSO, respectively[12]). However these pathways are not expected to be important, as the EPR spectra have not evidenced any other radical species, excepting the spin-adduct and an aminoxyl impurity with a_N of about 1.3 mT apparent only in ethereal solvents, especially when the peroxide impurities were not removed, and tentatively assigned to the trapping of superoxide radicals. The cation-radical of DMPO, DMPOox, for which $a_N = 0.67$ mT, was not detected, which represents further support for the idea that mechanism (2) leading to the spin-adduct is not operative in this case.

Kinetic studies

Because of the experimental difficulties already mentioned, reliable kinetic studies could be performed only in CCl$_4$ for the n–π* band of MTAD and in ACN, using the FT-IR data on the PTAD carbonyl band. As both solvents have no or difficult to abstract H-atoms, reaction (4a) can be neglected, as well as reaction (5b), which is highly improbable in the presence of RTAD, as already stated in the previous discussion. The proposed reaction mechanism may be synthesised as reactions (6)–(10), where A stands for RTAD, B for DMPO, AH$_2$ for urazole and AB for the reaction product.

$$\text{B} + \text{AH}_2 \xrightleftharpoons{K_1} \text{ABH}_2 \qquad (6)$$

$$\text{ABH}_2 + \text{A} \xrightleftharpoons{K_2} \text{ABH}^{\bullet} + \text{AH}^{\bullet} \qquad (7)$$

$$\text{AH}^{\bullet} + \text{B} \xrightarrow{k_1} \text{ABH}^{\bullet} \qquad (8)$$

$$\text{ABH}^{\bullet} + \text{AH}^{\bullet} \xrightarrow{k_2} \text{AB} + \text{AH}_2 \qquad (9)$$

$$\text{ABH}^{\bullet} + \text{A} \xrightarrow{k_3} \text{AB} + \text{AH}^{\bullet} \qquad (10)$$

With the steady state condition for ABH$^{\bullet}$, the rate of decrease of RTAD is given by:

$$-dA/dt = k_3[A] \frac{k_1[AH^\bullet][B]}{k_2[AH^\bullet] + k_3[A]}$$

If we suppose that reaction (10) is much slower than reactions (8) and (9), $k_3 \ll k_1, k_2$ and one obtains:

$$-dA/dt \cong k_1 k_3/k_2 [A][B] \cong k_{app}[A][B],$$

i.e. an approximate second order global kinetics.

Starting from different initial concentrations of RTAD and DMPO, best fitting for the reaction of MTAD with DMPO in CCl$_4$ followed in the n–π* band of MTAD (see Fig. 5) is obtained with $k_{app} = (17 \pm 2)$ l mol^{-1} s^{-1}. For the PTAD–DMPO system, the kinetics followed in the carbonyl band of PTAD at 1778 cm^{-1} led to $k_{app} = 7$ l mol^{-1} min^{-1}.

In conclusion it may be stated that in spite of the approximations used, the proposed mechanism for the reaction of triazolinediones with the nitrone spin-trap DMPO accounts reasonably well for the experimental data.

Experimental

4-Methyl-1,2,4-triazoline-3,5-dione (MTAD) and 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) were synthesised starting from the corresponding urazoles by literature methods.[15] DMPO was reagent grade from Aldrich, used without further purification.

The solvents (Aldrich) were dried over 3 Å molecular sieves; the ethers were eluted over a 20 cm alumina (neutral) column to eliminate the small amounts of peroxides.

The IR spectra were recorded on a Mattson 1000 FT-IR spectrometer and the UV–VIS spectra on a Unicam spectrometer. The NMR spectra were obtained using a Bruker 400 MHz spectrometer. EPR spectra were recorded on a JEOL JES-3B spectrometer in the X-band frequency, using peroxylamine disulfonate as standard ($g = 2.0055$, $a_N = 1.300$ mT). IR spectrum of the final reaction product **2** (KBr): v(cm^{-1}) 3428w (v_{N-H}), 2982w and 2949w (v_{C-H}), 1785m and 1730s (v_{C-O}), 1635m ($v_{>N-C\doteq N}$), 1606m, 1448s (v_{N-N}), 1395w, 1171m and 1026w ($v_{C-C, C-N, N-O}$), 750m, 622m.

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