

THALLIUM SENSITIZED PHOTOLYSIS OF NITRITE ION IN APROTIC SOLVENTS

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Summary

Solutions of various metal nitrites were illuminated by photons capable of promoting NO_2^- to its lowest singlet electronically excited state (n, π^*). No significant photolysis occurred for aqueous solutions of various univalent metal nitrites, including TlNO_2 , or for solutions of NaNO_2 in dimethylformamide (NaNO_2/DMF). Whenever Tl^+ ions also were present together with NO_2^- in DMF or in other aprotic solvents, greatly enhanced extinction coefficients and rates of photolysis were observed. The quantum efficiency $\Phi(-\text{NO}_2^-)$ rose to 0.3 for TlNO_2/DMF at 10^{-2} M and a parallel loss of thallium from solution accompanied nitrite photolysis. Results of spectroscopic studies are interpreted in terms of the enhanced charge transfer character of the $S_0 \rightarrow S_1$ transition in the presence of Tl^+ . The observed concentration dependence of the quantum yield arose mainly from bimolecular dissociation of charge transfer exciplexes at concentrations of 10^{-3} - 10^{-1} M. At low concentrations luminescence was detected from TlNO_2/DMF and from $\text{TlNO}_2/\text{CH}_3\text{CN}$ solutions but was quenched by NaNO_2 .

Introduction

An earlier communication from this laboratory [1] concluded, on the basis of markedly different quantum efficiencies for the formation of nitroxide radicals from solutions of the metal nitrites NaNO_2 , $\text{Ba}(\text{NO}_2)_2$, CsNO_2 or TlNO_2 irradiated *in situ* in an EPR spectrometer, that the stability of the first excited singlet state of the nitrite ion in dimethylformamide (DMF) was influenced by formation of solvent-separated or solvent-shared

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ion pairs. These EPR studies showed that NO_2 was not a detectable product from TINO_2/DMF . In the present study the ability of the heavy metal cation TI^+ to sensitize photolysis of NO_2^- via ion pair formation in aprotic solvents is confirmed through conventional photochemical experiments. These permit comparison of quantum efficiencies and kinetics for the loss of NO_2^- from illuminated solutions of TINO_2 in DMF with similar data for solutions of other univalent metal nitrites. Correlations are sought between these photochemical results and new spectroscopic data on NO_2^- obtained here by NMR, IR and UV-VIS studies on metal nitrite solutions mainly at concentrations 10^{-3} - 10^{-2} M. Particular attention is given in this study to possible correlations between the efficiency of nitrite photolysis and the extent of perturbation of the NO_2^- ion as deduced from spectroscopic measurements.

The bulk of existing spectroscopic data on the nitrite ion has been derived from studies on single crystals of NaNO_2 or other solids at low temperatures. Such studies have yielded detailed information on the bent configuration of the ion and on energy levels of its S_0 , S_1 and T_1 states [2 - 5]. It is generally agreed that the $S_0 \rightarrow S_1$ transition in pure NaNO_2 crystals is centred around 360 nm and results in $S_1 \rightarrow S_0$ fluorescence centred around 425 nm. A very weak $S_0 \rightarrow T_1$ absorption centred around 450 nm has been observed in nominally pure NaNO_2 crystals [4]. Garber and Reznik recently demonstrated a marked enhancement of this $S_0 \rightarrow T_1$ transition in crystals of NaNO_2 doped with TI^+ , Pb^{2+} or Ag^+ ions and considered the possible effects of charge transfer on the intensity and polarization of this transition [6]. In contrast, Maria *et al.* noted a long lived luminescence centred around 550 nm from crystals doped with heavy metals or from doped solutions frozen to a glass at 77 K [7]. They assumed that negligible $T_1 \rightarrow S_0$ phosphorescence occurred for the unperturbed nitrite ion but proposed that association of the anion with heavy metal cations resulted in enhanced intersystem crossing to the triplet state of NO_2^- which then emitted phosphorescence centred on 550 nm.

In addition to the quoted evidence for perturbation of the electronic transitions of NO_2^- by adjacent heavy metal cations in solid systems at low temperature, the literature also provides evidence for perturbation of such transitions by interactions of the nitrite ion with cations or solvent molecules in liquid solution. Thus Harris *et al.* have presented evidence for a large intensification of the $S_0 \rightarrow T_1$ transition at 450 nm in aqueous solutions of AgNO_2 [8]. Strickler and Kasha presented evidence that both $S_0 \rightarrow S_1$ transitions of type $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ respectively exhibited a blue shift of about 10 nm when measured in hydroxylic solvents (H_2O or EtOH) relative to aprotic solvents [9]. They claimed furthermore that the probability of another $n \rightarrow \pi^*$ transition (of symmetry ${}^1A_2 \leftarrow {}^1A_1$), which is forbidden by molecular symmetry for the undistorted NO_2^- ion, acquired measurable intensity in hydroxylic solvents through hydrogen bond formation but that such distortion did not occur in aprotic solvents. The present study attempts to establish the consequences of such perturbations for the photochemical stability of the NO_2^- ion in various solutions.

Experimental

Metal nitrites

Solutions were prepared from reagent grade metal nitrites where these were available, namely Proanalyse NaNO_2 (Merck), LiNO_2 (Lithium Corporation of America), CsNO_2 (K and K Laboratories), KNO_2 and $\text{Ba}(\text{NO}_2)_2$ (BDH), AgNO_2 (Research ROC/RIC Chemicals) and nitrogen-15 enriched $\text{Na}^{15}\text{NO}_2$ (Isomet Corporation). For $\text{Tl}^{15}\text{NO}_2$ or $\text{Tl}^{14}\text{NO}_2$, where the metal nitrite was not commercially available, solutions containing Tl^+ and NO_2^- were obtained by mixing a solution of $\text{Ba}(\text{NO}_2)_2$ with a solution of an appropriate thallium salt and filtering off the precipitated barium salt. An orange waxy solid, analysing as TlNO_2 , was isolated from such solutions by crystallization and was purified by recrystallization. The small quantities of $\text{Na}^{15}\text{NO}_2$ available did not permit separation of solid $\text{Tl}^{15}\text{NO}_2$ from solutions similarly prepared to contain Tl^+ and $^{15}\text{NO}_2^-$.

Solvents

High purity dimethylformamide (DMF), dimethylsulphoxide (DMSO) and hexamethylphosphortriamide (HMPT) obtained from Merck were used without further purification. Methyl cyanide (MeCN), ethanol (EtOH) or methanol (MeOH) solvents as obtained from BDH were dried and distilled prior to use in preparing solutions. Solutions were stored in actinic glassware to avoid degradation by sunlight. Spectra or photolyses were usually examined within 48 h of preparation. The only solutions which gave indications of instability of NO_2^- through loss of nitrite absorbance during 48 h storage were $\text{TlNO}_2/\text{HMPT}$, $\text{AgNO}_2/\text{DMSO}$ and AgNO_2/DMF .

Spectroscopic measurements

Nitrogen-15 NMR spectra on solutions containing $\text{Na}^{15}\text{NO}_2$ or ($^{15}\text{NO}_2^- + \text{Na}^+$ and Tl^+) were run on a Bruker-Spectrospin Fourier transform spectrometer at Queen Mary College, London, by courtesy of Dr. Farnell and Dr. Randall. Metal nitrite concentrations were about 0.1 M and yielded very weak signals that required signal averaging over 1 - 8 h in order to achieve acceptable signal to noise ratios. Perkin-Elmer 402 or Cary 14R double beam recording spectrometers were used to obtain electronic absorption spectra in the visible and near UV using quartz cells of path lengths 0.5 - 100 mm as appropriate. Infrared spectra were measured using AgCl or CaF_2 cells of path lengths 0.1 - 2 mm and Perkin-Elmer 257 or 457 IR spectrometers. Solutions were not de-aerated for these spectroscopic measurements and all spectra were recorded at ambient temperature. Frequencies of each observed absorption were calibrated by reference to external standards. The concentration dependence was studied only for electronic absorption spectra in the UV-visible range and apparent molar extinction coefficients ϵ'_c for each concentration c were derived from application of the Beer-Lambert equation.

Preliminary measurements of luminescence from TlNO_2 at concentrations 10^{-4} - 10^{-1} M in DMF were made with a Corning-Eel commercial

fluorometer using excitation at 380 nm and a solvent reference to correct for any luminescence from the solvents. Relative efficiencies of luminescence were attempted by comparison with solutions of quinine sulphate having similar optical density (OD) at 370 nm in order to equalize "inner filter" effects.

Comparison of sensitivities towards photolysis by light of $\lambda > 300$ nm

Use of the intense emission at 366 nm from a 500 W Hg lamp for investigating the relative sensitivities of TINO_2 and NaNO_2 solutions towards photolysis was justified by the close proximity of this Hg emission line to the λ_{max} reported (about 370 nm for these nitrites in DMF [1] or 355 nm in water [9]). Photolyses of de-oxygenated solutions were performed by simultaneously irradiating several solutions of metal nitrites contained in Pyrex glass vessels symmetrically arranged around the water cooled 500 W mercury arc lamp. In order to achieve good mixing, to exclude oxygen and to sweep away any gaseous products a steady flow of oxygen free nitrogen gas (saturated with the vapour of the solvent being used and broken up by a fritted disc into a stream of fine bubbles) was established through each solution for over 15 min prior to illumination and was maintained throughout illumination. Unless otherwise stated, light incident onto the samples was restricted to the wavelength region 340 - 640 nm by the use of a Wratten 38A gelatin filter wrapped around the water cooled lamp housing. This ensured that light incident onto the solutions of metal nitrites was sufficiently energetic to promote only transitions from the singlet ground state to the lowest singlet or the lowest triplet states (transitions reported respectively at about 360 and 475 nm [3]). Nitrite ion concentrations of the illuminated solutions were selected to give initial absorbances of about 1.0 for a 1 cm path length at the maximum of the $S_0 \rightarrow S_1$ transition at 330 - 400 nm. After illumination of duration 1 - 6 h, aliquots were withdrawn and their optical absorption spectra recorded in the range 300 - 500 nm. Absorbance at λ_{max} of the $S_0 \rightarrow S_1$ transition of NO_2^- in that solvent (about 360 nm) served to monitor any photochemically induced changes in the NO_2^- concentration in these aliquots relative to blank samples which were similarly purged with N_2 but were not illuminated.

Measurements of thallium concentration

Aliquots of TINO_2/DMF or $\text{TINO}_2/\text{H}_2\text{O}$ solutions were analysed for Tl^+ on a Pye Unicam SP 191 atomic absorption spectrophotometer using the thallium resonance line at 276.8 nm and a 0.2 nm spectral bandpass. Prior to assay, each solution of TINO_2/DMF was diluted with water so as to reduce Tl^+ to about 20 ppm. Calibrations established linearity and high sensitivity towards Tl^+ in that concentration range, with reproducibility to ± 1 ppm for runs on different days.

Quantum efficiencies

Quantum efficiencies for the loss of nitrite or loss of Tl^+ from illuminated TINO_2/DMF solutions were determined from initial rates of loss of nitrite

absorbance at 370 nm or of Tl^+ seen by atomic absorption. A narrow-bandpass filter (355 - 375) with maximum transmission at 365 nm and secondary filters to eliminate IR was utilized to admit only the Hg resonance band at 365 nm from a 250 W compact Hg-Xe arc lamp to the magnetically stirred Pyrex photolysis cell. The photon flux was monitored with a potassium ferrioxalate actinometer.

Results and discussion

Spectroscopic studies on metal nitrite solutions

Infrared spectra

The three normal vibrational modes for the bent NO_2^- ion have been assigned as ν_1 at ~ 1330 , ν_3 at ~ 1240 and ν_2 at $\sim 815\text{ cm}^{-1}$ [2, 10]. Aprotic solvents used in this study had an IR "window" in the $750 - 900\text{ cm}^{-1}$ region and so permitted (with some difficulty) studies on the ν_2 bending mode. Previous studies had indicated that the frequency of this mode increased to about 870 cm^{-1} when the nitrite existed in strong nitrito-type complexes involving metal coordination to oxygen and to 840 cm^{-1} for nitro-type complexation of metal to nitrogen [10, 11].

Results summarized in Table 1 show that only for $Cd(NO_2)_2$ and $AgNO_2$ in KBr discs or for saturated solutions of $AgNO_2$ in MeCN or DMF did our IR measurements give evidence for the existence of NO_2^- mainly as nitrito- or nitro-type complexes. In order to obtain sufficiently strong absorbance it was necessary to use saturated solutions (about 0.2 M for $TlNO_2/DMF$) in the 0.5 mm AgCl or NaCl cells. Occurrence of the main IR absorption by NO_2^- at 810 cm^{-1} for saturated solutions of $NaNO_2$ or $TlNO_2$ in DMF or DMSO and a similar main peak position for $Ba(NO_2)_2$ in DMF provided convincing evidence that strongly bonded nitro- or nitrito-type complexes were not the dominant species, even at the largest attainable concentration of those metal nitrites. It is important to note, however, that these observations would not rule out the possibility that nitrite existed in the aprotic solvents mainly as "weak" complexes, such as "solvent-shared ion pairs" or as weakly bonded complexes of the type recently suggested for thallium nitrate [12]. The presence of weak shoulders (see Table 1) on the main ν_2 peak pointed to the existence of some nitrite ions having force constants significantly modified by cation interactions.

NMR

Signal averaging over 8 h of operation of the NMR spectrometer at 9.12 MHz which was locked to a D_2O reference yielded narrow singlet NMR lines with signal to noise ratio greater than or equal to 10 and with positions reproducible to ± 3 Hz (Fig. 1(a)). Measurements on $Na^{15}NO_2$ solutions demonstrated the occurrence of down-field shifts by 80 ± 6 Hz in resonance position when the solvent was altered from H_2O to any of the aprotic solvents HMPT, DMSO or DMF. This corresponded to an apparent chemical shift of 9 ppm on changing from hydroxylic to aprotic solvent.

TABLE 1

Position of ν_2 mode absorption for metal nitrites in KBr discs and aprotic solvents

Medium	Nitrite					
	NaNO ₂	LiNO ₂	TlNO ₂	AgNO ₂	Ba(NO ₂) ₂	Cd(NO ₂) ₂
KBr disc	829	—	808	808 840	820	850
DMF ^a	810	—	810	837 (819) ^c	805 (794) ^c	n.s.s. ^b
DMSO ^a	805	805	810	n.s.s. ^b	800	n.s.s. ^b
MeCN ^a	n.s.s. ^b	820	820 (800) ^c	835	—	n.s.s. ^b

^aMeasured on saturated solutions in dry dimethylformamide, dimethylsulphoxide or methyl cyanide.

^bDenotes that metal nitrite was not sufficiently soluble to yield reliable IR absorption.

^cNumbers in parentheses denote position of shoulders on main ν_2 band with $(25 \pm 10)\%$ of its intensity.

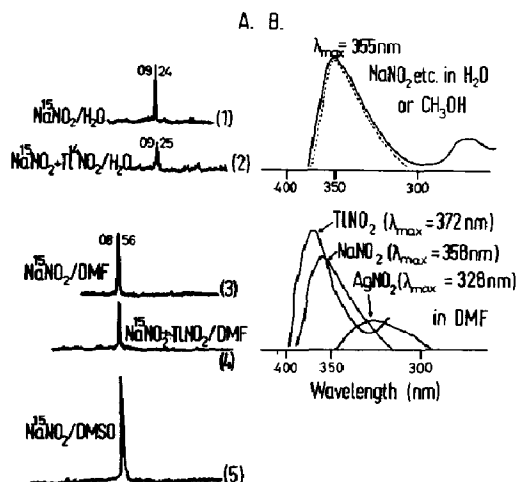


Fig. 1. NMR and UV-VIS spectra illustrating solvent induced shifts for metal nitrites in aprotic solvents. (A) Position of nitrogen-15 NMR resonance observed for (1) saturated aqueous solution of Na¹⁵NO₂, (2) equimolar aqueous solution of Na¹⁵NO₂ and Tl¹⁴NO₂, (3) saturated solution of Na¹⁵NO₂ in dimethylformamide, (4) as for (3) but with addition of Tl¹⁴NO₂ and (5) saturated solution of Na¹⁵NO₂ in dimethylsulphoxide. (B) Position of the $n \rightarrow \pi^*$ absorption band in the UV-VIS range for (upper plots) metal nitrites dissolved in H₂O or CH₃OH and (lower plots) metal nitrites dissolved in dimethylformamide.

With aqueous solutions of Na¹⁵NO₂ no measurable shift in position of the ¹⁵NO₂⁻ resonance was observed when TlNO₂ was introduced to equimolar concentration, thereby demonstrating that chemical shifts due to possible ion pairing with Tl⁺ must be smaller than those observed to arise from varia-

tions in ion-solvent interactions. With DMF or DMSO as solvent, no shift greater than 3 Hz was observable owing to interactions with Tl^+ in ion pairs. A small downfield shift equivalent to about 1 ppm did, however, accompany the introduction of $TlNO_2$ into a solution of $Na^{15}NO_2$ in HMPT.

UV-visible spectra

Preceding NMR and IR observations characterized any Tl^+ interaction with NO_2^- as weak since they indicated that hydroxylic solvents exerted a stronger perturbing influence on the ground state of NO_2^- than could be achieved by ion pairing to cations other than Ag^+ or Cd^{2+} in aprotic solvents. Ultraviolet-visible absorption spectra of various 10^{-3} M metal nitrite solutions, including $AgNO_2$ in MeCN, were carefully examined for evidence of corresponding perturbations of electronic transitions between ground and electronically excited states of NO_2^- . Figure 1(B) illustrates typical spectra. Results obtained in this study of values for λ_{max} and ϵ'_{max} for the electronic transition(s) responsible for optical absorption at 300 - 400 nm are summarized in Table 2. Data therein illustrate the following salient features.

(a) Data in the first two data columns on λ_{max} in CH_3OH and water, which were selected as representative hydroxylic solvents, demonstrate the absence of any significant ($> \pm 1$ nm) shift either on changing between these solvents or on changing the cation. These data, like the NMR data, are thus consistent with the view that hydroxylic solvents strongly solvate the nitrite ion and effectively exclude cations from the anion solvation sheath, so that ion pair interactions remain undetectable in hydroxylic solvents at the submolar concentrations used in this study.

(b) Data on λ_{max} in columns 5 - 8 of Table 2 were obtained with polar aprotic solvents using identical spectroscopic techniques to those employed for hydroxylic solvents but are very much more variable with the nature of the solvent or of the cation. With the exception of $AgNO_2$, these λ_{max} values for aprotic solvents lie in the range 363 ± 13 nm. The large blue shift (about 30 nm) of λ_{max} for solutions of $AgNO_2$ relative to this mean value for the other metal nitrites in the same aprotic solvent represents further evidence for significant perturbation of the ground state or of the first excited singlet state of NO_2^- through interactions with Ag^+ . Although the smaller and irregular variations in λ_{max} of this band with the nature of the other cations are not fully understood, the contrast between them and the definite blue shift obtained with $AgNO_2/CH_3CN$ makes it improbable that strong ion pair complexes exist for those other metal nitrite solutions. However, the data do not rule out the possibility of solvent-shared ion pairs or other weak complexes existing between nitrite and Tl^+ or other cations in the aprotic solvents.

(c) It emerges from values of ϵ' in Table 2 that only solutions of $AgNO_2$ or $TlNO_2$ showed large variations in ϵ' with choice of solvent. At concentrations of 10^{-3} M, ϵ'_{max} is seen to be an order of magnitude greater for $TlNO_2$ in DMF or CH_3CN than in CH_3OH or water as solvent. The increase in ϵ'_{max} is greatest for the aprotic solvent of the lowest dielectric constant (DMF ~ 26.7) studied, thereby suggesting role(s) for electrostatic interaction and/or charge

TABLE 2

Spectroscopic data on 10^{-3} M solutions of metal nitrites: parameters of near UV absorption (320 - 400 nm)

Salt	Parameter ^a	Hydroxylic solvents			Aprotic solvents			
		H ₂ O ($D = 81$) ^c	CH ₃ OH ($D = 32.6$) ^c		HMPT	DMSO ($D = 46.6$) ^c	CH ₃ CN ($D = 37.5$) ^c	DMF ($D = 26.7$) ^c
LiNO ₂	λ_{\max}	355	-		350	370	345	360
	ϵ'_{\max}	-	-		25	28		27
NaNO ₂	λ_{\max}	355	-		357	362	360	358
	ϵ'_{\max}	-	-		29	29	20	28
KNO ₂	λ_{\max}	355	355		364	370	367	364
	ϵ'_{\max}	21	-		28	30		28
CsNO ₂	λ_{\max}	355	-		375	372	365	372
	ϵ'_{\max}	-	-		26	25	-	21
Ba(NO ₂) ₂	λ_{\max}	356	356		364	365	-	376
	ϵ'_{\max}	22	-		40	35	-	39
TlNO ₂	λ_{\max}	356	356		370	372	368	3372
	ϵ'_{\max}	23	30		50 ^b	60	180	200
AgNO ₂	λ_{\max}	355	Insoluble		330	334	332	328
	ϵ'_{\max}	17	-		-	60 ^b	Sat. solv. only	12 ^b

^a λ_{\max} is expressed in nm with an error of ≤ 2 nm; ϵ'_{\max} is expressed as $M^{-1} \text{ cm}^{-1}$.^bSome evidence of instability was noted for these solutions in the dark.^c D is the dielectric constant.

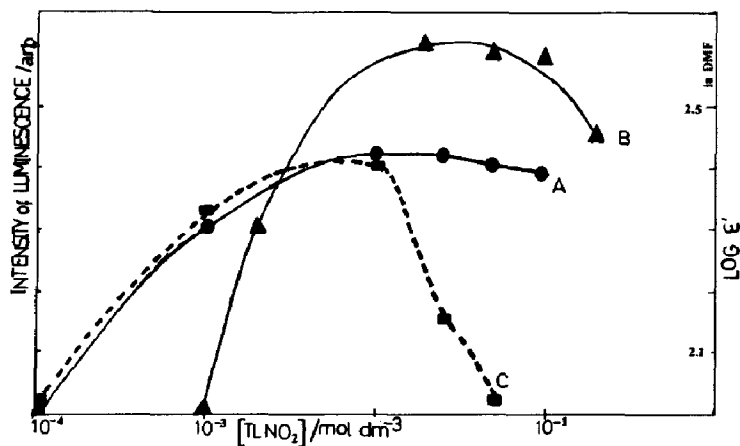


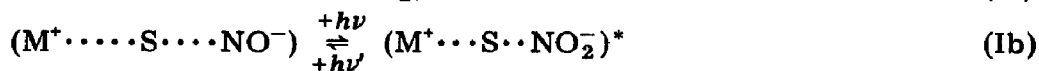
Fig. 2. The concentration dependence of absorption and luminescence from solutions of TiNO_2 in aprotic solvents: curve A, variations of the apparent value ϵ' of the extinction coefficient for optical absorption at $\lambda = 372 \text{ nm}$ for solutions in DMF; curve B, as for curve A except with DMSO as solvent; curve C, variations of the observed intensity of the luminescence with a maximum at 470 nm under excitation at 380 nm .

transfer in enhancing ϵ'_{max} for TiNO_2 dissolved in aprotic solvents. On the basis of the now accepted electron affinity of 2.4 eV for NO_2 [13] and a value of 6.1 eV for the ionization potential of Ti^0 , partial transfer of the electron from NO_2^- towards Ti^+ would certainly be energetically feasible with the excited NO_2^- (S_1^*) state and may possible occur in the ground state if the combined solvation energies of Ti^+ and NO_2^- in DMF are less than 3.7 eV . (It is of interest to note that electron transfer from Ti^+ towards NO_2^- would be energetically unfavourable either in the ground or excited state.)

Curve A of Fig. 2 presents results of measurements made on the extinction coefficient ϵ'_{max} of TiNO_2/DMF solutions at various concentrations $10^{-4} - 10^{-1} \text{ M}$. The reality of the apparent maximum value of $265 \text{ l mol}^{-1} \text{ cm}^{-1}$ observed at added TiNO_2 equivalent to 10^{-2} M was confirmed by measurements on three series of solutions. These marked variations in ϵ_{max} in curve 2 represent strong evidence for the existence of anion-cation complexes in these solutions and they furthermore suggest a gradual increase in concentration of one ion pair complex, species D, in dilute solutions at $10^{-4} - 10^{-2} \text{ M}$, giving way at higher concentrations to another complex, species C, with a lower extinction coefficient. Ion pair formation at low concentrations and the onset of ion cluster formation at higher concentrations have been proposed to explain concentration induced changes in IR spectra of silver nitrate in methyl cyanide [14].

Exploratory studies of luminescence from TiNO_2/DMF solutions over this range of concentrations under excitation at 380 nm readily showed measurable emission at concentrations $10^{-3} - 5 \times 10^{-2} \text{ M}$, with λ_{max} of the luminescence at 470 nm . Curve C of Fig. 2 illustrates that the concentration dependence of the signal output from the Corning-Eel fluorometer for various

TiNO₂/DMF solutions strongly resembled the concentration dependence of ϵ'_{\max} (compare curve C with curve A). These observations on absorbance and luminescence increasing at concentrations 10⁻⁴ - 10⁻² M could be understood if these processes related, as in (Ib), to solvent-shared ion pairs whose equilibrium concentration varied with concentration according to (Ia):



An association equilibrium constant K_a should describe the variation with TiNO₂ concentration of species D, identified as a solvent-shared ion pair, (Ti⁺⋯S⋯NO₂⁻). The semi-empirical model of Fuoss for the equilibrium between free ions and ion pairs for a 1:1 electrolyte yielded the expression $K_a = 4\pi N a^3 e^b / 3000$, in which a corresponds to the ion pair diameter, $e = 4.8 \times 10^{10}$ e.s.u., N is Avogadro's number and b is given by $Z_a Z_b e^2 / aDKT$. Taking the dielectric constant D of DMF as 26.6 at $T = 298$ K, the value of b applicable to these TiNO₂/DMF solutions may be calculated as 4.2 if an ion pair diameter of 5×10^{-8} cm is assumed [15]. An estimated value of 21 could thus be arrived at for ion pair association between univalent ions on the basis of coulombic interaction only. This value was an order of magnitude lower than an alternative estimate for K_a of about 300 derived from analysis of absorbance data according to the Benesi-Hildebrand method (see succeeding paragraph). Furthermore the estimates of extent of coulombic ion pairs based on K_a of about 21 increased continuously from 0.05 at 10⁻³ M to 0.14 at 10⁻² to 10⁻¹ M. It was therefore concluded that, although the Fuoss model may provide useful estimates for the extent of the coulombic ion pair formation from NaNO₂/DMF, it is not adequate to describe ion pair formation in TiNO₂/DMF. Interactions other than coulombic must exist between Ti⁺ and NO₂⁻ in that system. Further evidence in support of this conclusion came from observations that, upon adding NaNO₂ in increasing excess to 10⁻² M TiNO₂/DMF, the absorbance increased to a greater extent (20 - 30% greater) than predicted on the basis of ϵ_{\max} remaining unchanged at 270 and 21 l mol⁻¹ cm⁻¹ for TiNO₂ and NaNO₂ respectively.

Since charge transfer between NO₂⁻ as donor and Ti⁺ as acceptor was a likely form of additional interaction, the Benesi-Hildebrand expression was applied to absorbance data in the manner described by Carter [16]. This required use of data from solutions with excess of donor (NO₂⁻) over acceptor (Ti⁺), which were readily obtained by measurements on solutions with [Ti⁺] fixed at 10⁻² M but with increasing excess of [NaNO₂]. The Benesi-Hildebrand expression in the form

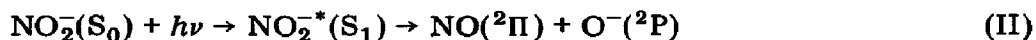
$$\frac{[Ti^+]_0 l}{Abs'_{370}} = \frac{1}{K'_{DA} \epsilon_{370}} \frac{1}{[NO_2^-]} + \frac{1}{\epsilon_\lambda} \quad (1)$$

was therefore applied to such data in an attempt to derive values for the equilibrium constant K'_{DA} for donor-acceptor pair formation in the ground

state and for ϵ_{370} , the effective extinction coefficient for such complexes at 370 nm. An approximation was needed to obtain values for the absorbance Abs'_{370} by the donor-acceptor complex at 370 nm from measured absorbance and was made by subtracting an absorbance of uncomplexed nitrite calculated on the basis of the $\epsilon = 21 \text{ l mol}^{-1} \text{ cm}^{-1}$ value observed for NaNO_2/DMF . The linear plot which resulted from application of eqn. (1) to the experimental data extrapolated to a value of $\epsilon_{370} \sim 500 \text{ l mol}^{-1} \text{ cm}^{-1}$ for infinitely high donor concentration. A limiting value for K'_{DA} of about 300 l mol^{-1} resulted from this analysis. Such values would correspond to extensive occurrence of donor-acceptor pairs in these solutions. However, other spectroscopic data indicated that the extent of such charge transfer must be very small or that its relaxation time must be very short in the TINO_2/DMF solutions at room temperature. Thus the solutions gave no measurable ESR signal in the dark, and neither the NMR nor IR spectra would be consistent with nitrite existing largely as NO_2 -type species. Furthermore the value for ϵ'_{370} of about $500 \text{ l mol}^{-1} \text{ cm}^{-1}$ derived above is two orders of magnitude below that expected for donor-acceptor pairs forming with large charge transfer [17].

Photochemical studies

Unimolecular photodissociation of non-solvated nitrite ion to non-solvated products via the reaction



would be allowed by spin conservation. However, an energy requirement of about 390 kJ mol^{-1} may be estimated using a cycle based on 300 kJ mol^{-1} for NO_2 photodissociation [17] and electron affinities of 230 and 140 kJ mol^{-1} for $\text{NO}_2(^2\Pi)$ and $\text{O}(^2P)$ respectively [18 - 20]. Process (II) in an aprotic solution may thus not be energetically feasible with photons of λ greater than 310 nm. The horizontal line plots in Fig. 3 confirm that no loss of nitrite absorbance occurred when solutions of $\text{TINO}_2/\text{H}_2\text{O}$ or NaNO_2/DMF were illuminated in conditions which limited incident light to photons with λ greater than 340 nm. Nitrite concentration was in all cases monitored by absorbance of the solutions of λ_{max} of the nitrite band at about 370 nm. Other plots in these figures illustrate that, whenever the thallos ion was substituted in whole or in part for the alkali metal cation, significant loss of nitrite occurred in aprotic solutions exposed to this illumination, namely TINO_2/DMF , $\text{TINO}_2/\text{DMSO}$ or admixtures of $(\text{TINO}_2 + \text{NaNO}_2)/\text{DMF}$. Figure 3(a) summarizes results demonstrating a readily measurable loss of absorbance by the nitrite ion ($\lambda_{\text{max}} = 372 \text{ nm}$, $\epsilon'_{\text{max}} = 280$) from rigorously deoxygenated solutions of TINO_2/DMF when these were illuminated by the output of the 500 W Hg arc lamp filtered through a Wratten 38A gelatine filter (transmitting 340 - 640 nm). Comparison of the plot for TINO_2 dissolved in H_2O as a hydroxylic solvent with that for TINO_2 in the aprotic solvents DMF or DMSO show that only for the latter solvents was there any appreciable illumination induced loss of nitrite absorbance. Figure 3(B) demonstrates

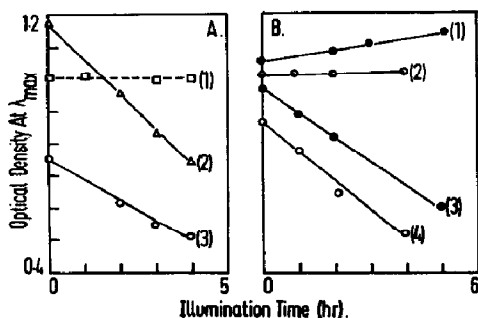
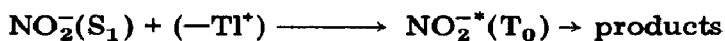


Fig. 3. Effect of 350 - 640 nm illumination on the nitrite absorbance (optical density) for solutions of $TlNO_2$ in various solvents or with admixtures of $NaNO_2$. (A) The influence of solvent on the rate of photolysis illustrated for (1) $TlNO_2/H_2O$, (2) $TlNO_2/DMF$ and (3) $TlNO_2/DMSO$. (B) The rate of photolysis for varying Tl^+/Na^+ ratios for solutions of $TlNO_2$ and/or $NaNO_2$ in DMF illustrated for (1) $NaNO_2/DMF$, (2) $NaNO_2:TlNO_2 = 3.3$, (3) $NaNO_2:TlNO_2 = 1$ and (4) pure $TlNO_2$.

that illumination of solutions of $NaNO_2/DMF$ in similar conditions to those employed for $TlNO_2/DMF$ did not produce any loss of nitrite absorbance. Similar experiments with solutions of $NaNO_2/H_2O$ or $KNO_2/MeCN$ demonstrated that no photolysis occurred. These qualitative comparisons established that thallium sensitized the photolysis of nitrite relative to similar solutions of sodium or potassium nitrite but that it did so only in aprotic solvents. This sensitization is well illustrated by plots (2), (3) and (4) of Fig. 3(B) which demonstrate that the rate of an apparently linear decrease of nitrite absorbance with illumination increased with the ratio of Tl^+ to Na^+ for DMF solutions of $NaNO_2$ and/or $TlNO_2$. The apparently zero order dependence of rate on nitrite concentration in these plots originated from their large initial absorbance and concentrations and was not an intrinsic kinetic feature of the sensitized photolysis. This became clear from more detailed kinetic studies performed at lower nitrite concentrations, which were undertaken in an attempt to discriminate between the following broad categories of interaction, involving the excited nitrite ion and Tl^+ as likely origins of the thallium sensitized photolysis:

(A) conversion to product via thallium promoted crossover to triplet



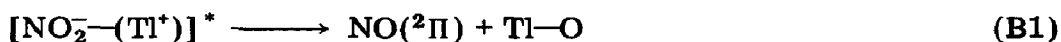
(B) conversion to product following exciplex formation with Tl^+



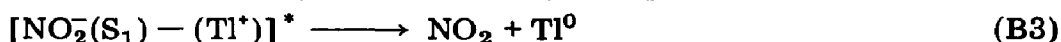
The notation $(-Tl^+)$ as used in these equations may indicate either cations bound to nitrite ion in solvent-shared ion pairs at the instant of excitation or cations encountered by NO_2^* through diffusion during its lifetime. The notation $[NO_2^-(S_1)-Tl^+]^*$ used to denote an ion pair exciplex does not exclude the possibility of large charge transfer in the formation of this excited ion pair.

The possibility that process (A) contributed significantly to thallium sensitized photolysis was eliminated by results of observations made with incident photons restricted to wavelengths longer than 400 nm through use of a Wratten 40A filter. With this light the process of optical excitation was limited to direct formation of $\text{NO}_2^*(\text{T}_0)$ through absorption in the thallium promoted $\text{S}_0 \rightarrow \text{T}$ transition having λ_{max} at 450 nm. No illumination induced loss of nitrite was observed from TINO_2/DMF (or $\text{TINO}_2/\text{MeCN}$) in these conditions. The contrast between this lack of photolysis following thallium promoted excitation of NO_2 into its triplet state and the rapid photolysis observed under excitation at 365 nm pointed to an essential role of $\text{NO}_2^*(\text{S}_1)$ in thallium sensitized photolysis by type (B) processes. Singlet ion pair exciplexes might, however, contribute to thallium promoted nitrite photolysis by any of the following mechanisms:

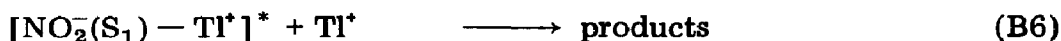
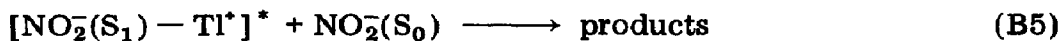
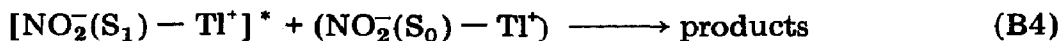
(1) unimolecular reaction within exciplexes



(2) irreversible charge transfer through exciplex dissociation



(3) bimolecular interaction of exciplexes with ground state ions or ion pairs



Ideally it should be possible by kinetic analysis to distinguish (B1), (B2) and (B3), which would be first order in $[\text{NO}_2^-(\text{TI}^*)]^*$, from (B5) and (B6), which would have additional first order dependence upon $[\text{NO}_2^-]$ and $[\text{TI}^+]$ respectively, or from (B4) which should be second order in the ion pair concentration. Photolyses of TINO_2/DMF were therefore carried out to high percentage decomposition with a view to establishing order of reaction by kinetic analysis of the decay of nitrite absorbance. Plot A of Fig. 4 illustrates that, within appreciable error limits, a second order plot was consistent with the data so obtained. The data were not adequately represented by a first order plot.

One factor contributing to the appreciable experimental error in measurements on photo-assisted loss of absorbance at 370 nm from the 10^{-2} M TINO_2/DMF solutions was the growth of a white precipitate during illumination. This contributed errors through light loss by scattering. However, this photo-assisted precipitation of a thallium-rich solid (analysis showed it to contain over 80% thallium) made it possible to follow the course of photolysis by monitoring the residual thallium content of the solutions. This was done with an atomic absorption spectrophotometer upon liquid aliquots

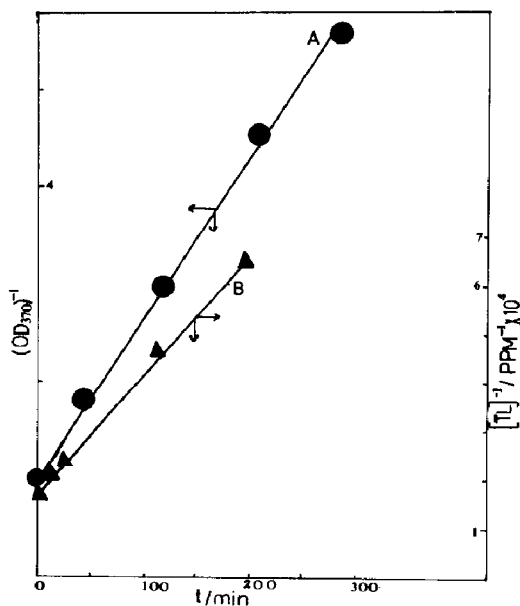
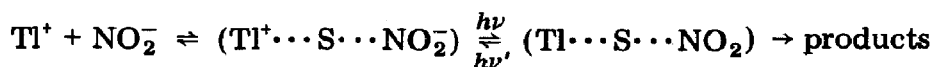


Fig. 4. Plots demonstrating the second order kinetic behaviour for loss of nitrite absorbance or of Tl^+ from solutions of TlNO_2 in DMF under illumination at 366 nm: plot A, loss of nitrite absorbance monitored at 372 nm; plot B, loss of Tl^+ monitored by atomic absorption.

taken at intervals from the illuminated TlNO_2/DMF solutions and centrifuged or filtered prior to analysis. Plot B of Fig. 4 illustrates that a second order plot was consistent, again within appreciable experimental scatter, with the photo-assisted removal of thallium from 10^{-2} M TlNO_2/DMF .

For reasons already stated, data from extensive photolysis did not lend themselves to precise kinetic analysis. Consequently, quantum yields for photo-assisted loss of nitrite absorbance or of thallium from solutions illuminated at 370 nm were determined from the rate of loss during an initial 1 - 5% photolysis. These values are summarized in Table 3(a) for measurements based on the initial rate of loss of nitrite absorbance and in Table 3(b) for measurements based on the initial rate of loss of thallium from the illuminated solutions. The marked concentration dependence of both sets of quantum efficiencies, with an order of magnitude increase between 10^{-3} and 10^{-2} M TlNO_2 , provides strong supporting evidence for the essentially bimolecular nature of the final dissociative step of the overall scheme:



Processes (B4), (B5) and (B6) are bimolecular in nature and could account for the observed concentration dependence as originating from diffusion controlled dissociative encounters between other components of the solution and ion pair exciplexes with lifetimes about 3×10^{-8} s. This estimate of radiative lifetime can be arrived at [21] on the basis that about 5% of the exciplexes suffering dissociation at 10^{-3} M TlNO_2 via the above scheme, but

TABLE 3(a)

Estimates of quantum efficiency based on nitrite absorbance loss in solutions of TlNO_2 in DMF

$[\text{TlNO}_2]$ (M)	ϵ_{370}^a ($\text{l mol}^{-1} \text{ cm}^{-1}$)	ΔOD_{370} ($\text{cm}^{-1} \text{ h}^{-1}$)	$\Phi(-\text{NO}_2)^b$
10^{-3}	200	0.055	0.06
5×10^{-3}	243	0.115	0.08
10^{-2}	260	0.5	0.30

^a ϵ_{370} denotes apparent molar extinction coefficient at 370 nm.

^b $\Phi(-\text{NO}_2)$ calculated from initial rates of loss of nitrite absorbance at a photon flux of $2.1 \times 10^{16} \text{ photons s}^{-1}$.

TABLE 3(b)

Estimates of quantum efficiency based on the loss of thallium concentration as monitored by atomic absorption spectrophotometry in solutions of TlNO_2 in DMF

$[\text{TlNO}_2]$ (M)	$\Delta[\text{Tl}]^+$ (ppm h^{-1})	$X(\text{Tl}^+)$	$\Phi(-\text{Tl}^+)$
10^{-3}	10^a	0.05	0.01
10^{-2}	308^a	0.15	0.26
5×10^{-2}	2667	0.26^b	2.1^b

$X(\text{Tl}^+)$ denotes fraction of total thallium removed (per hour).

^aDenotes initial rate of loss of Tl^+ as calculated from the slope of the concentration vs. photolysis time graph.

^bThese values are subject to large error owing to the initially high value of $[\text{Tl}^+]$ and the large dilutions needed.

it is likely to represent an upper limit since radiationless processes are not taken into account in the scheme.

Preliminary evidence of competition between radiative and non-radiative processes emerged from studies of the influence of added NaNO_2 upon the efficiency of luminescence or of photolysis for solutions originally 10^{-3} M or 10^{-2} M in TlNO_2 . Luminescence was decreased by such additions whereas efficiency of photolysis was not observed to increase significantly.

The quantum efficiencies recorded for $10^{-3} - 5 \times 10^{-2} \text{ M}$ solutions in Table 3 indicate, even when allowance is made for larger experimental error attached to the measurements of small changes in initially large values of nitrite absorbance or $[\text{Tl}^+]$, that $\Phi(-\text{Tl}^+)$ increased more rapidly with initial concentration than did $\Phi(-\text{NO}_2)$. This effect could be understood if at the higher concentrations photo-initiated charge transfer to thallium resulted in $(\text{Tl}_n)^{+m}$ clusters rather than monatomic Tl^+ . For the analogous $\text{AgNO}_3/\text{MeCN}$ system, where ion clusters exist at high concentrations, Symons *et al.* [22] have proposed Ag_2^+ and Ag_4^{3+} as products of the major electron capture process under γ irradiation. Irreversible charge transfer yielding thallium clusters may at higher concentration also contribute to the observed decrease in luminescence.

Conclusion

The spectroscopic results presented here for solutions of thallium nitrite in DMF and DMSO can be satisfactorily explained in terms of the existence of weak charge transfer ion pairs which undergo a thallium enhanced transition to a singlet excited ion pair state possessing greater charge transfer character. Luminescence from this state can be observed at low concentrations (10^{-3} M) but at higher concentrations the charge transfer ion pair exciplex dissociates via bimolecular interaction with ground state ion pairs or with Tl^+ .

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