The Origin and Nature of Chemiluminescence in the Dibenzoylperoxide-Dimethylaniline Reaction

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Key Words: Chemical Kinetics / Chemiluminescence / Elementary Reactions / Radicals

It has been established that the dibenzoylperoxide (POOP)+dimethylaniline (DMA) reaction is suitable to the slow production of free radicals at ambient temperature and in the absence of oxygen. The process is accompanied by a well measurable chemiluminescence (CL) without added sensitizer. The reaction carried out in acetonitrile is mainly ionic with the formation of radicals in between. We assume the existence of a 2:1 DMA/POOP complex as a possible source of radicals. The kinetics of CL is determined by the formation and decomposition rate of this complex. Calculated rate constant values: $k_{(f)} = 3 \times 10^{-3}\ M^{-1}\ s^{-1}$ and $k_{(d)} = 1 \times 10^{-3}\ s^{-1}$. Based on the spectrum of the CL light and taking into consideration the analytical results we assume that the energy of CL is delivered almost totally by the cage termination product ($\Delta H_{(r)} = -385$ kJ/mol) formed in excited state and this energy is transferred to the triphenylmethane dye-salt products (Malachite Green, Crystal Violet) which are the probable emitters of the CL light. Hydroperoxide is not formed in the reaction.

1. Introduction

Recently it has been suggested [1] that the interaction of excited triplet state sensitizers with free radicals (triplet-doublet interactions) under in vivo conditions might contribute essentially to overall photodynamic effects. Though both in vitro and in vivo experiments have supported this assumption [2, 3], direct measurements yielding quantitative kinetic results are either missing or refer only to changes in the lifetime of the excited sensitizer molecules as a result of the interactions [4].

According to literature data [5–8] such interactions have been studied in detail with sensitizers not used in biology or with stable free radicals as partners. Therefore, it seemed expedient to carry out investigations in a chemical model system where biologically active sensitizers are applied, transition free radicals are formed and their interactions can be followed by sensitive experimental methods, as e.g. chemiluminescence measurements.

The following requirements can be put forward concerning the model system: (i) free radicals generated by a chemical process at ambient temperature should give measurable chemiluminescence (CL); (ii) generation of free radicals should proceed in the absence of oxygen in order to avoid the reaction between triplet sensitizer and oxygen molecules competing with the triplet-doublet processes to be followed; (iii) based on our previous investigations and literature data formation of hydroperoxide molecules in the overall chemical reaction should not take place since triplet sensitizers attack such molecules [9, 10] and thus the triplet-doublet interaction would be masked. Literature data [11–16] indicate that the reaction of dimethylaniline with dibenzoylperoxide might fulfil all the requirements described above and although many papers have been published concerning this reaction only two of them [14, 15] mention that it is accompanied by CL light emission. Since it is well known that CL is the light emission of an excited (singlet or triplet) molecule formed in a highly exothermic elementary process (e.g. termination of radicals or annihilation of ion-pairs) the present paper reports results on CL measurements as well as product studies carried out with respect to this system. (Throughout the paper the abbreviations already introduced by Horner [11] are used being closely related to the structure of molecules.)

2. Experimental Section

2.1 Materials

'Chemolab' HPLC grade acetonitrile (AN), 'Reanal' dimethylsulfoxide (DMSO) purified by freezing and 'Merck' benzene (Uvasol) were used as solvents.

'Fluka' dibenzoylperoxide (POOP), 2,6-di-tert.-butyl-p-cresol (BHT), 'Aldrich' 1-naphtol were used without further purification, 'Reanal' dimethylaniline (DMA) was distilled after treatment with acetic anhydride.

HPLC standards for identification: 'Sigma' N-methyl-formanilide (OHC-MA), 4,4′-bis-(dimethylamino)benzhydrol ($(DMA)_2CHOH$), 4-dimethylamino-benzaldehyde (DMA-CHO), N,N,N′,N′-tetramethyl-benzidine (TMB); 'Aldrich' 4,4′-bis-(dimethylamino)benzophenone ($(DMA)_2CO$), benzoic anhydride (POP), 4-dimethylamino-benzophenone; 'Fluka' methylbenzoate (CH_3-OP), Crystal Violet chloride (CV); 'Merck' benzil, Malachit Green oxalate (MG), Methyl Violet 2B chloride (MV); 'Reanal' methylaniline (MA), benzoic acid (POH), benzaldehyde (B-CHO) were used without further purification and leuco-crystal violet (LCV) [17], 4,4′-bis-(dimethylaminodiphenyl)methane ($(DMA)_2CH_2$) [18], phenyl-benzoate (Ph-OP) [19] were synthesized according to the literature given.

2.2 Methods

CL kinetics and spectra were measured by a home-built, computer controlled fiberoptics chemiluminescence

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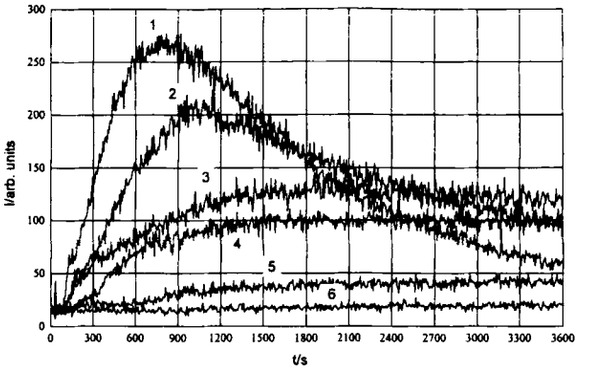


Fig. 1
CL versus time in AN and nitrogen atm., $T=298$ K, $[POOP]_0=1\times10^{-2}$ M, $[DMA]_0$: $1=2\times10^{-1}$ M, $2=1\times10^{-1}$ M, $3=5\times10^{-2}$ M, $4=2\times10^{-2}$ M, $5=1\times10^{-2}$ M, $6=2\times10^{-3}$ M

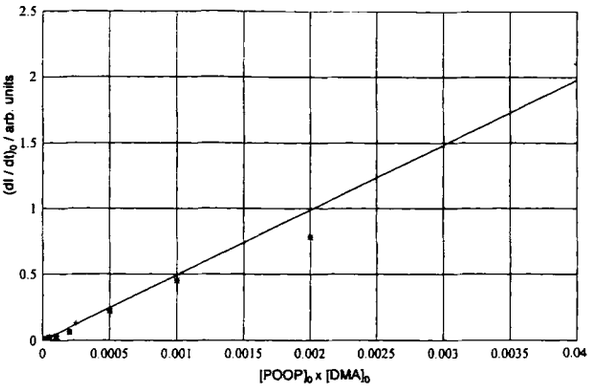


Fig. 2
Dependence of $(dI/dt)_0$ on $[POOP]_0\times[DMA]_0$, 298 K, nitrogen atm. ×: $[POOP]_0=1\times10^{-2}$ M, ▲: $[DMA]_0=2\times10^{-2}$ M, +: $[DMA]_0/[POOP]_0=10$, –: linear regression

spectrometer (Type VG-06) described previously [20]. An Hp 8452A Diode Array Spectrophotometer was used for taking UV-VIS kinetics and spectra. Specific conductance was measured with a conductivity meter (Radelkis, Type OK-102/1) using a Pt bell-electrode.

Product analyses have been carried out by HPLC (250×4 mm C-18 reverse column, Milton-Roy pump, CE-CIL CE 212 UV detector at 235 nm, eluent 60/40 methanol/pH 7 phosphate buffer, 1 ml/min [20min] and 1.5 ml/min [40 min]) and partly by GC-MS (Finnigan GCQ).

Experiments have been performed at room temperature. The initial amount of POOP (0.002–0.02 M) dissolved in 4–4.5 ml solvent (AN, DMSO, AN-DMSO mixture or benzene) was placed into the reaction vessel and deoxygenated in situ with nitrogen (99.99%) purified with alkaline pyrogallol. A few minutes later reaction has been commenced by adding appropriate amounts of DMA (0.002–0.2 M) dissolved in 1–0.5 ml solvent. The total voulme of the sample was always 5 ml.

3. Results and Discussion

3.1 Chemiluminescence of the DMA-POOP System

Several runs of experiments have been performed to observe the effect of varying the $[DMA]_0/[POOP]_0$ ratio and the total amounts of the reagents used at constant $[DMA]_0/[POOP]_0$ ratio on the CL kinetics. Since the intensity of the CL light is well measurable in itself no sensitizer was applied. The influence of the $[DMA]_0/[POOP]_0$ ratio on the CL curve is shown in Fig. 1.

It can be seen that a CL curve going through a maximum (which has been observed already by Vasil'ev et al. [14]) appears only at $[DMA]_0/[POOP]_0$ ratios higher than or equal to unity. The statistical evaluation of $(dI/dt)_0$ obtained from three different runs clearly shows (Fig. 2) – taking into account the ±10% error of measurements – that they are proportional to $[DMA]_0/[POOP]_0$.

This agrees well with the observations described in the literature [21, 22]. Compiling the maximal intensity (I_{max}) and the corresponding time (t_{max}) data and plotting them against the $[DMA]_0/[POOP]_0$ ratio (Fig. 3) it can be seen that there is an explicit change in the trends of both curves around 2. Increasing the ratio from 0 to 2, I_{max} and t_{max} are changing steeply in opposite direction but this change is slowing down above 2 being almost linear up to 20. This can be due to a change in the mechanism around the ratio $[DMA]_0/[POOP]_0=2$.

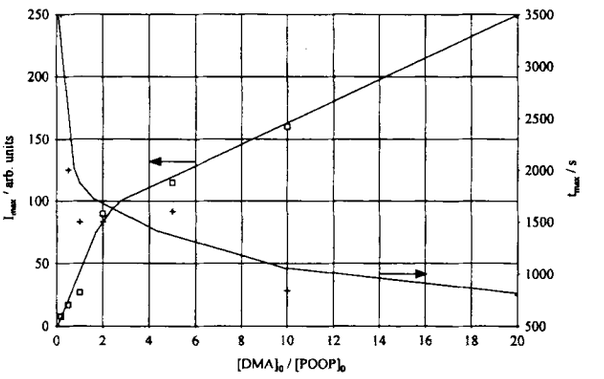


Fig. 3
I_{max} and t_{max} as a function of the $[DMA]_0/[POOP]_0$ ratio

It should be noted that at the end of the reaction the reaction mixture colourless initially became reddish violet and the intensity of this colour was dependent on the initial concentration of the reactants and on the time elapsed. Graham and Mesrobian [23] observed a similar phenomenon in the oxidation of DMA catalyzed by POOP and recently Senel et al. [24] established that the bulk homogeneous polymerization of ethyl methacrylate initiated by the POOP-DMA redox pair became more or less red depending on the amount of DMA used.

3.2 CL Measurements in the Presence of Radical Scavengers

BHT and 1-naphtol (the same amount as $[DMA]_0$) added to the reaction mixture after I_{max} (Fig. 4) leads to a

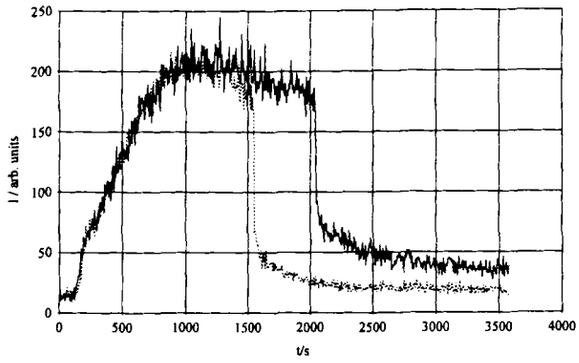


Fig. 4
Effect of inhibitors on the CL kinetics, 298 K, nitrogen atm., $[POOP]_0 = 1\times10^{-2}$ M, $[DMA]_0 = 1\times10^{-1}$ M, (–) = 1×10^{-1} M BHT, (- -) = 1×10^{-1} M 1-Naphtol

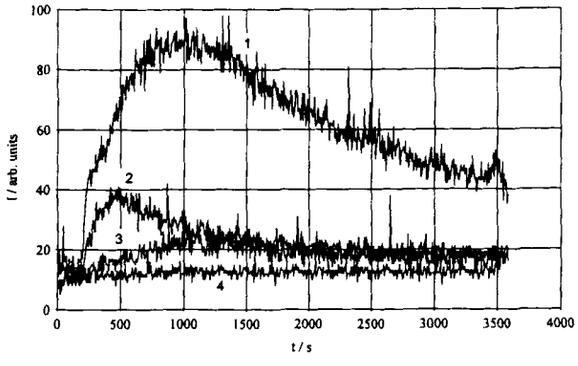


Fig. 5
Effect of BHT added initially on the CL. 298 K, nitrogen atm., $[POOP]_0 = 1\times10^{-2}$ M, $[DMA]_0 = 1\times10^{-1}$ M, $[BHT]_0$: $1 = 1\times10^{-3}$ M, $2 = 5\times10^{-3}$ M, $3 = 1\times10^{-2}$ M, $4 = 1\times10^{-1}$ M

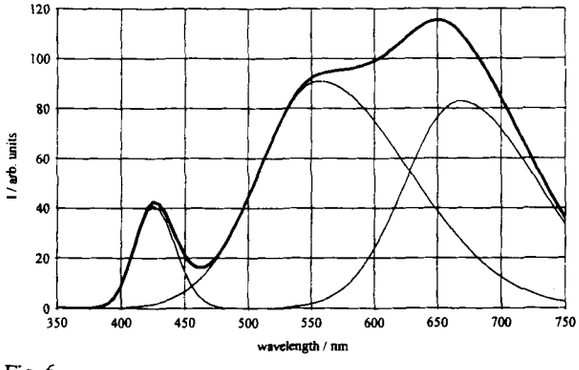


Fig. 6
Corrected and normalized CL spectrum of 1×10^{-2} M POOP+1×10^{-1} M DMA in AN, 298 K, nitrogen atm. –: sum of the three individual peaks

fast decrease to 20–25% of the original CL intensity followed by a much slower decay. If we inject BHT (equal to $[POOP]_0$) after different time intervals the percentage decrease of intensity is independent of the time of addition. The CL curves with different amounts of BHT added initially to the system are depicted in Fig. 5. In contrast to the inhibited polymerization or other free radical chain reactions no inhibition period can be observed. Instead the area under the CL intensity curve is decreasing – while the maximum still exists – as $[BHT]_0$ is aproaching $[DMA]_0$. If the $[BHT]_0$ equals $[DMA]_0$ no CL signal can be observed at all. Taking into consideration that the radical efficiency of the DMA-POOP reaction is only 0.1–0.2 (in apolar solvents [25, 26]) and no inhibition period could be observed it is very likely that the termination of radicals occurs mostly within the cage and therefore CL arises from this cage-termination. Thus for scavenging all the radicals formed the DMA molecules must be substituted entirely by inhibitor molecules in the shell of the cage. In other words, there exists a preferential solvation of the POOP molecules by DMA and inhibition of CL can be achieved only if $[BHT]_0 \geq [DMA]_0$.

3.3 Spectrum of the CL Light

CL spectra were taken with a series of cut-off filters (370–715 nm) during kinetic CL measurements. The histogram obtained has been evaluated by a Gauss curve fitting computer program and at the same time it was corrected for the change of the CL intensity during the measurement. The CL spectrum (Fig. 6) although structureless indicates that the CL light consists of a blue and a red region. The blue peak ($\lambda_{max} \approx 430$ nm) is small and comparatively narrow, while the two red ones ($\lambda_{max} \approx 560$ and 670 nm) are very intense and broad. In the case of hydrocarbon oxidation the blue CL corresponds mostly to the light emission of an excited keton or aldehyde formed in a highly exothermic (>300 kJ/mol) reaction but in the DMA-POOP reaction the formaldehyde formed is not a termination product [27]. According to Zupancic et al. [28] singlet oxygen is not formed in this reaction and since there is no oxygen present in the system the red part of the CL spectrum might be of another origin.

3.4 Solvent Dependence of the CL Kinetics

According to literature data [13, 16, 22, 29–31] the reaction has a strong ionic character especially in AN and it has been observed [23] that it proceeds much faster in polar solvent (e.g. in AN) than in apolar ones. The use of 10–20% of DMSO was expedient since porphyrin-derivatives to be used in the future cannot be dissolved in AN. Therefore CL kinetics has been measured in AN-DMSO mixtures ranging from 0 to 100% DMSO. Fig. 7 shows the dependence of the initial intensity change of CL against solvent composition. It should be mentioned that in neat DMSO only an initial burst can be observed followed by negligible CL light afterwards.

Experiments carried out in benzene as solvent showed that the reaction is accompanied also by the emission of CL light exhibiting a maximum but the overall rate of the reaction is about seven times smaller and therefore I_{max} is lower and t_{max} is about seven times larger than in AN. This means that radical processes are dominating and ionic ones (which are mainly the DMA consuming

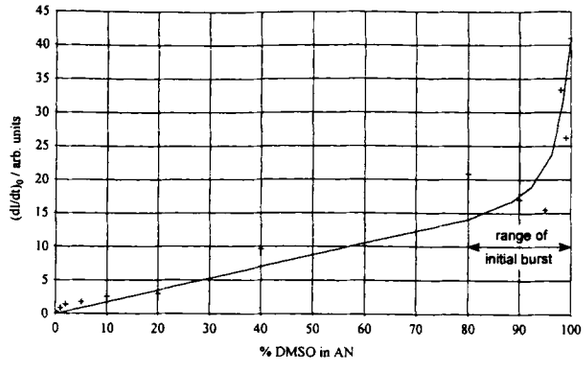


Fig. 7
Dependence of $(dI/dt)_0$ on the solvent composition at 298 K in nitrogen atm. $[POOP]_0 = 1\times10^{-2}$ M, $[DMA]_0 = 1\times10^{-1}$ M

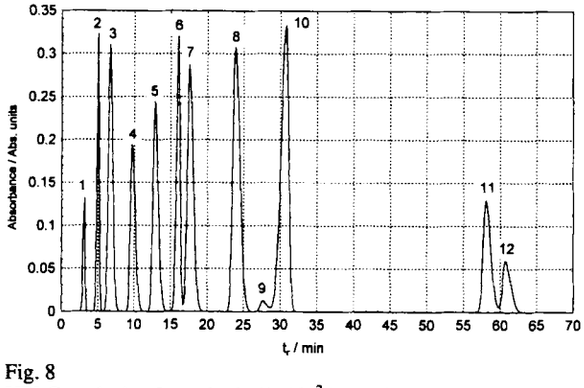


Fig. 8
HPLC analysis of standards (1×10^{-3} M each) in CH_3OH/buffer (pH 7) 60/40%, 235 nm. Retention times: 1: POH (3.1′), 2: MA–CHO (5′). 3: MA (6.6′), 4: $POCH_3$ (9.7′), 5: DMA (11.6′). 6: $(DMA)_2CHOH$ (16.5′), 7: benzil (17.5′)), 8: Ph–OP /23.8′), 9: POP (27.6′), 10: POOP (30.8′), 11: $(DMA)_2CH_2$ (58.5′), 12: TMB (60.7′)

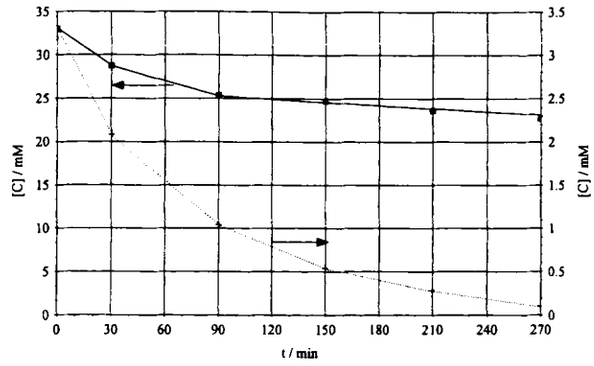


Fig. 9a
Consumption of reactants followed by HPLC in the reaction of 3.3×10^{-3} M POOP+3.3×10^{-2} M DMA in AN, nitrogen atm., 298 K. ■ = DMA (left ord.), + = POOP (right ord.)

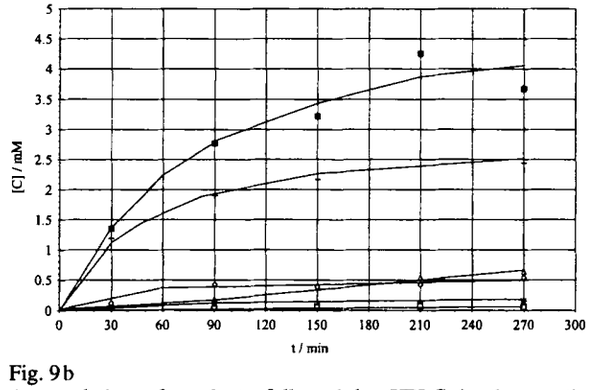


Fig. 9b
Accumulation of products followed by HPLC in the reaction of 3.3×10^{-3} M POOP+3.3×10^{-2} M DMA in AN, nitrogen atm., 298 K. ■ = POH, + = MA, * = $POCH_3$, □ = Benzi, × = $(DMA)_2CH_2$, △ = OHC–MA

secondary condensation reactions) are strongly suppressed in this apolar solvent. The solution becomes only pale yellow.

4. Product Studies by HPLC and UV-VIS Spectrophotometry

HPLC separation method has been worked out for the quantitative determination of products formed in the DMA-POOP reaction. Very good separation has been achieved by using a methanol/pH 7 phosphate buffer mobile phase as it can be seen in Fig. 8. But water-sensitive compounds (e.g. benzoic anhydride) and CV, MV and MG cannot be analyzed in this mobile phase.

Special runs have been carried out for the HPLC analysis in rubber stoppered vials where the reaction took place under nitrogen atmosphere. The initial concentration chosen for DMA and POOP enabled us to withdraw samples with a syringe in every hour (which corresponds to the time of analysis) loading it after diluted ten-times by AN immediately into the sample loop, since the reaction cannot be stopped even in diluted samples.

Fig. 9a represents the consumption of the starting materials, Fig. 9b the accumulation of identified products. Two non identified products have been observed just before and after the peak of POOP (retention time (t_r): 26.4 and 33.1 min). Identification of N-methyl-formanilide (OHC-MA) among the products (both by HPLC and GC-MS) was an important information. It is evident from Fig. 9a that the consumption of DMA exceeds three-times that of POOP. Fig. 9b shows that most of the POH and MA ($+CH_2O$) are probably primary products while the other four formed only in smaller amount are secondary ones.

The kinetics of the formation of CV+MV (they cannot be distinguished in the very similar and superimposed bands around 600 nm) and of MG has been followed by UV-VIS kinetic spectrophotometry in the 300–700 nm range using 10×10 mm stoppered cuvettes (see Fig. 10). These dyes are formed obviously via ionic condensation of aldehydes with DMA or MA. Since neither DMA and POOP nor the products of the reaction – including CV and MV – have absorption in the 400–430 nm region this peak can be assigned to the low wavelength absorption of MG.

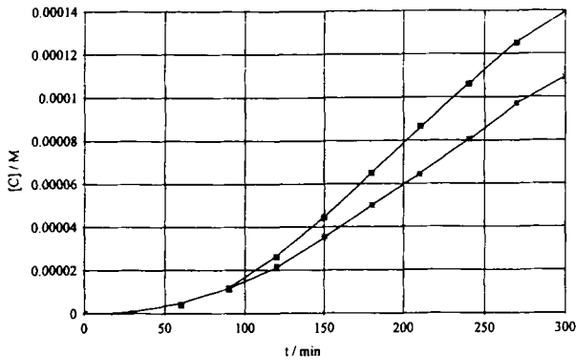


Fig. 10
Accumulation of CV and MG followed by UV-VIS spectrophotometry in the reaction of 3.3×10^{-3} M POOP+3.3×10^{-2} M DMA in AN, nitrogen atm., 298 K

5. Supplementary Measurements in the POOP-DMA Reaction

To learn more about the ionic character of the reaction specific conductivity has been measured in AN solution using 1×10^{-3} M concentration of each reactants and products available. The reaction mixture has also been measured after 5 h. It has been established that the specific conductivity of the latter increased during this time period from 1 to 115 μS and this value is comparable only with the specific conductivity measured with the dyes MG and CV. Only 1–4 μS was obtained with the rest of compounds.

6. The Suggested Mechanism of the POOP-DMA Reaction in AN

Based on experimental results and literature data an attempt has been made to compile the mechanism of the process. Since the heats of reaction (ΔH_r) are important informations to identify the possible CL light emitter(s) processes include this values (in kJ/mol) too. Formulation of radicals and ions are also represented by "Horner's type" symbols, e.g.:

$$DMA^{\bullet} = (CH_3)_2N - C_6H_4^{\bullet};$$
$$^{\bullet}DMA = {}^{\bullet}CH_2N(CH_3) - C_6H_5 \quad \text{and}$$
$$PO^{\bullet} = C_6H_5 - C(O) - O^{\bullet};$$
$$P = C_6H_5 - C^{\bullet}(O) \quad \text{and}$$
$$PO^{-} = C_6H_5 - C(O)O^{-}$$

Though according to Pryor and Hendricksen [16] the process starts with an SN_2 reaction and Walling and Indictor [13] established that there is no kinetic evidence of a pre-equilibrium the question is still unanswered: which atom is the target of the nucleophil attack in the POOP molecule? Denney and Denney [31] published experimental results using POOP labeled with O^{18} in the carbonyl-groups and proved that the carbonyl-labeling remained practically unchanged in the course of the reaction, that is the attack of DMA takes place on the peroxidic oxygen. This does not exclude the possibility described by Sakai et al. [32] performing ab initio calculations for the DMA-POOP system and concluded that the lone-pair of electrons on the nitrogen in DMA attack the C-atom of the C=O group in the POOP.

Let us assume that both processes are taking place. This means that complexes of two different structures are formed in the first step and their decomposition leads to the formation of different products.

If the nucleophil attack occurs on the peroxidic oxygen [16, 29, 31] the large endothermicity of reaction (1) being in contradiction with the warming up of the reaction mixture observed already by Horner et al. [11] makes it unlikely.

$$DMA + POOP \rightarrow Complex\,(O) \rightarrow PO^{-} + PO^{\bullet} + (CH_3)_2\overset{\bullet+}{N} - C_6H_5$$
$$\Delta H_r = 598 \qquad (1)$$

Based on the analogy with the reaction of triphenylphosphine (Φ_3P) and POOP [33] we assume that this step is a purely ionic one resulting in the formation of DMA-N-oxide (DMANO) and POP.

$$DMA + POOP \rightarrow \{Complex(O)\} \rightarrow DMANO + POP$$
$$\Delta H_r = -51 \qquad (2)$$

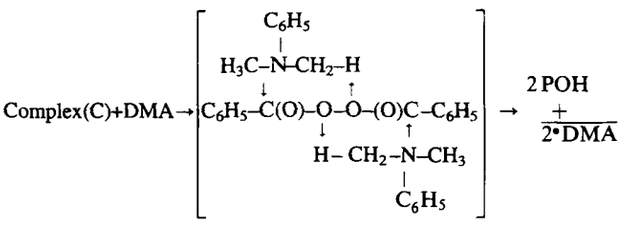
The formation of N-oxide in case of the thermal decomposition of POOP in pyridine [34] and in the oxidation of DMA [35] also supports this assumption.

If the target of DMA is the C-atom of the carbonyl-group a six-membered ring results directly in the formation of POH and PO-DMA in an exothermic reaction. This reaction is also an ionic one.

$$DMA+POOP \rightarrow \left[\begin{array}{c} C_6H_5\text{–}C(O)\text{–}O\text{–}O\text{–}C(O)\text{–}C_6H_5 \\ \uparrow \qquad\qquad \downarrow \\ CH_3\text{–}N\text{–}CH_2\text{–}H \\ \downarrow \\ C_6H_5 \end{array}\right] \rightarrow POH+PO\text{–}DMA$$

$$\{Complex(C)\} \qquad \Delta H_r = -255 \qquad (3)$$

The next step in compiling the mechanism of the DMA-POOP reaction is to find the way leading to the formation of radicals. According to literature data [24–26] and our CL measurements in the presence of radical inhibitors there is no doubt about the existence of this pathway but taking into account the results obtained for the dependence of I_{max} and t_{max} on the DMA/POOP ratio we have to assume that a third complex should also be formed from Complex(C) by the addition of a second DMA molecule. From sterical reasons and due to the slight endothermicity of reaction (4) the rate of this reaction must be smaller than that of reactions (2) or (3).



{Complex(C2)} $\Delta H_r = 104$ (4)

The formation of Complex(C2) assumed explains also the deceleration of the overall reaction experienced in apolar solvent (benzene) since the formation of radicals occurs only after two ionic steps.

According to Hrabak et al. [25] the fate of the radicals strongly depends on the medium (cage-effect) and on the solvation of radicals. They found that the induced decomposition of POOP is a chain reaction in benzene with a kinetic chain length of 10. Our finding that in AN as solvent this radical pathway does not lead to radical chain reaction agrees with that of Akopjan et al. [15].

$\overline{2^{\bullet}DMA} \rightarrow AMD - DMA(AMD - DMA^{*})$

$\Delta H_r = -385$ (5)

or

$\overline{2^{\bullet}DMA} \rightarrow 2^{\bullet}DMA$ (5a)

If 80–90% of the •DMA radicals terminate within the cage (reaction 5) where * denotes the molecule formed in excited state) only a small fraction of free radicals take part in the first propagation cycle represented by reactions (6, 7)

$POOP +^{\bullet} DMA \rightarrow PO - DMA + PO^{\bullet}$

$\Delta H_r = -241$ (6)

$PO^{\bullet} + DMA \rightarrow POH +^{\bullet} DMA(DMA^{\bullet})$

$\Delta H_r = -13(+37)$ (7)

Since most of the DMA-radicals formed in reaction (7) also terminate before attacking POOP a second propagation cycle can already be neglected. (The kinetic chain length in AN is about 1.) So it can be expected that the main termination product is AMD-DMA [29] and TMB [27] and cross-termination product (DMA-DMA) [30] are formed in negligible amounts. (Reaction (5) and (8) are identical apart from the cage.)

$2^{\bullet}DMA \rightarrow AMD - DMA(AMD - DMA^{*})$

$\Delta H_r = -385$ (8)

$2\,DMA^{\bullet} \rightarrow TMB(TMB^{*})$ $\Delta H_r = -498$ (9)

$^{\bullet}DMA + DMA^{\bullet} \rightarrow DMA - DMA(DMA - DMA^{*})$

$\Delta H_r = -436$ (10)

Termination reactions (5, 8, 9, 10) are sufficiently exothermic for the production of excited molecules which could serve as the energy source of CL light. It is known [36] that singlet excited TMB exhibits strong fluorescence in AN with a maximum at 405 nm but this can be red-shifted to 425–430 nm due to the presence of different molecules. Besides, the two other termination product could also take part in the development of the blue fluorescence observed. For explaining the red fluorescence observed the formation of energy acceptors can be assumed excited by energy transfer and their red fluorescence would correspond to the CL spectrum.

It was well known already hundred years ago [39] that the decomposition of DMANO leads to the formation of MA and CH_2O and this latter reacting with excess DMA yields $(DMA)_2CH_2$ found among the products [29, 40, 41].

$DMANO \rightarrow MA + CH_2O$

$\Delta H_r = -105$

$CH_2O + DMA \rightarrow DMA - CH_2OH$

$\Delta H_r = -43.5$ (12)

$DMA - CH_2OH + DMA \rightarrow (DMA)_2CH_2 + H_2O$

$\Delta H_r = -69.4$ (13)

Furthermore the large amount of DMA-OP found among the products (20–30%) [27, 29] could not be formed in a termination reaction. It is more likely that the intramolecular migration of the PO-group in the PO-DMA molecule (ionic reaction) leads to the formation of DMA-OP.

$PO - DMA \rightarrow DMA - OP$ $\Delta H_r = 2.55$ (14)

PO-DMA seems to be an important intermediate in the overall reaction because another type of intramolecular transformation (catalyzed by H^+) could yield benzaldehyde and N-methyl-formanilide since reaction (15) is nearly thermoneutral.

$PO - DMA \rightarrow OHC - MA + B - CHO$

$\Delta H_r = 2.88$ (15)

OHC-MA already mentioned by Schmidt et al. [42] as a product in the oxidation of tertiary amine has been found among the products by HPLC and identified by GC-MS. Benzaldehyde formed also in reaction (15) could react directly with excess DMA yielding leuco-MG.

$$B - CHO + 2\,DMA \rightarrow (DMA)_2 - CH - C_6H_5 + H_2O$$
$$\Delta H_r = -96.7 \quad (16)$$

Lindsay Smith et al. [37] and Grodowsky et al. [38] found that CV and MV are formed in the oxidation of DMA due to secondary condensation reactions between highly reactive product molecules and excess DMA. The OHC-MA formed in reaction (15) is a well known formylating agent [43] and reacting with DMA could yield DMA-CHO.

$$OHC - MA + DMA = DMA - CHO + MA$$
$$\Delta H_r = 43 \quad (17)$$

Further condensation of DMA-CHO with DMA yields a common intermediate which reacts either with DMA or with MA leading to the formation of leuco-CV and leuco-MV, respectively.

$$DMA - CHO + DMA \rightarrow (DMA)_2CHOH$$
$$\Delta H_r = -20 \quad (18)$$

$$(DMA)_2CHOH + DMA \rightarrow (DMA)_3CH + H_2O$$
$$\Delta H_r \sim -76.7 \quad (19)$$

$$(DMA)_2CHOH + MA \rightarrow (DMA)_2CH - AM + H_2O$$
$$\Delta H_r \sim -76.8 \quad (20)$$

Reactions (16, 19, 20) are responsible partly for the surplus consumption of DMA and POOP since the latter oxidizes leuco-dyes to the corresponding dye-salts:

$$(DMA)_2 - CH - C_6H_5 + POOP \rightarrow MG^+PO^- + POH$$
$$\Delta H_r = -141 \quad (21)$$

$$(DMA)_3CH + POOP \rightarrow CV^+PO^- + POH$$
$$\Delta H_r = -138.5 \quad (22)$$

$$(DMA)_2CH - AM + POOP \rightarrow MV^+PO^- + POH$$
$$\Delta H_r = -141 \quad (23)$$

Lewis et al. [44, 45] stated that CV^+ exhibits a green (at 90 K) and a red (at 160 K) phosphorescence but only in solid AN solution and this is true also for MV^+ both having 3 auxochromes and therefore should be excluded as possible energy acceptors and CL emitters. At the same time MG^+ has only two auxochromes [46] and thus the difference between the two degenerate singlet states (625 and 425 nm) supports our assumption that this is the probable emitter of CL. It has a red luminescence maximum at 670 nm [48] and a green phosphorescence at 467 nm [45]. The latter can not be observed in our system. Although the energy of the excited termination products is sufficiently large to produce excited MG^+ the mode of energy transfer is not clear at present. Since excited ions are not sensitive either to oxygen- or self-quenching [49] this also corresponds to the experimental observations.

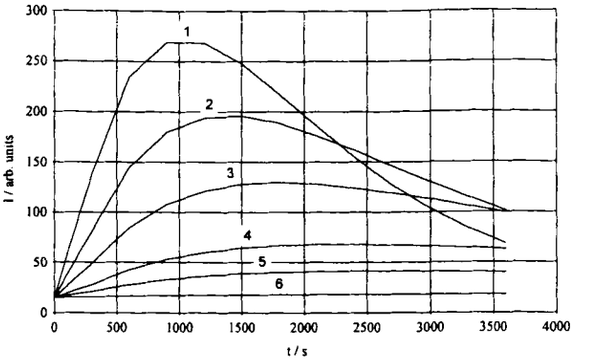


Fig. 11
Simulated CL kinetics of the DMA+POOP reaction. Concentrations and numbering of curves are the same as in Fig. 1

Although the existence of other secondary reactions (e.g.: oxidation of $(DMA)_2CH_2$ by POOP may be a second route leading to the formation of triphenylmethane dyes or in case of $[DMA]_0/[POOP]_0 \leq 1$ the reaction proceeds with the oxidation of the MA formed) cannot be excluded the mechanism described above is sufficient to compile the scheme of the reaction and could serve as a basis for computer simulation of experimental results.

7. Computer Simulation of Experimental Results

Reactions (1–23) completed with an appropriate set of rate constants (see Appendix) served as a basis of calculation which was performed by the ACUCHEM computer program. Only overall second order rate constants for the consumption of DMA and POOP are available from the literature [13, 16, 22, 25, 26] ranging from 5×10^{-4} to $5\times10^{-3}\ M^{-1}\ s^{-1}$. Rate constant for the radical termination and propagation reactions have been estimated by analogy while the rate constants for the other reactions were adjusted to fulfil the requirements given by the analysis of products. The best fit which has been found for the overall consumption rate constant of the DMA+POOP reaction was $6\times10^{-3}\ M^{-1}s^{-1}$. The rate determining step of the radical formation pathway is the formation and decomposition of the Complex(C2) with the calculated rate constants of $3\times10^{-3}\ M^{-1}s^{-1}$and $1\times10^{-3}\ s^{-1}$. Besides the kinetics of product accumulation are in agreement with the HPLC data. The CL kinetics calculated is represented by Fig. 11 for comparison with Fig. 1.

Calculations showed that DMA probably has a strong quenching effect and this must be taken into consideration.

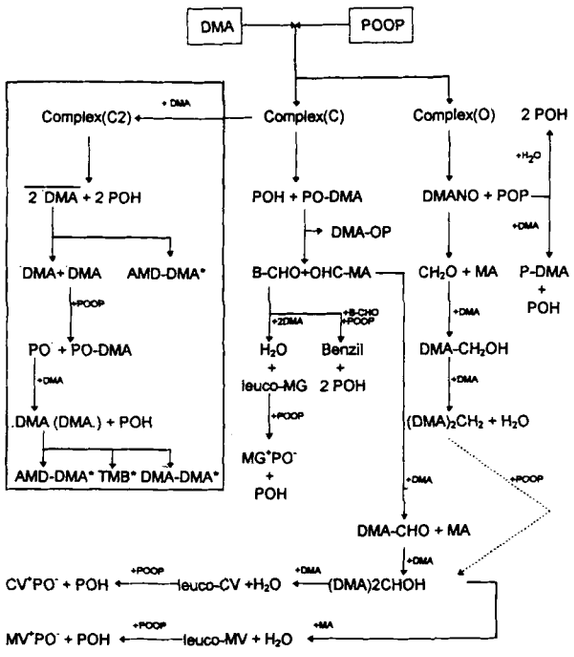
No. of reaction	Chemical processes	Rate constant (M^{-1} s^{-1})	Notes
2	DMA+POOP=K(O)	3.75×10^{-3}	
2a	K(O)=DMANO+POP	4×10^{-2}	a)
3	DMA+POOP=K(C)	2.25×10^{-3}	
3a	K(C)=POH+PO–DMA	1×10^{-2}	a)
4	K(C)+DMA=$\underline{K(C_2)}$	3×10^{-3}	
4a	$\underline{K(C_2)}$=2 POH+$\overline{2^{\bullet}DMA}$	1×10^{-3}	a)
5	$\overline{2^{\bullet}DMA}$=AMD–DMA(AMD–DMA*)	1×10^{9}	
5a	$\overline{2^{\bullet}DMA}$=$^{\bullet}$DMA+$^{\bullet}$DMA	2.5×10^{8}	
6	$^{\bullet}$DMA+POOP=PO–DMA+PO$^{\bullet}$	2×10^{1}	b)
7	PO$^{\bullet}$+DMA=POH+$^{\bullet}$DMA	1×10^{-1}	
7a	PO$^{\bullet}$+DMA=POH+DMA$^{\bullet}$	3×10^{-2}	
8	2$^{\bullet}$DMA=AMD–DMA(AMD–DMA*)	1×10^{9}	
9	2DMA$^{\bullet}$=TMB(TMB*)	1×10^{9}	
10	$^{\bullet}$DMA+DMA$^{\bullet}$=DMA–DMA(DMA–DMA*)	1×10^{9}	
11	DMANO=MA+CH_2O	1×10^{0}	a, b)
12	CH_2O+DMA=$DMACH_2OH$	8×10^{-3}	
13	$DMACH_2OH$+DMA=$(DMA)_2CH_2+H_2O$	3×10^{-2}	
14	PO–DMA=DMA–OP	5×10^{-3}	a)
15	PO–DMA=B–CHO+OHC–MA	1.2×10^{-2}	a)
16	B–CHO+DMA=B–CHOH–AMD	1.4×10^{-3}	
16a	B–CHOH–AMD+DMA=leuco–MG+H_2O	4.5×10^{-3}	
17	OHC–MA+DMA=DMA–CHO+MA	2×10^{-3}	
18	DMA–CHO+DMA=$(DMA)_2CHOH$	1×10^{-1}	
19	$(DMA)_2CHOH$+DMA=leuco–CV+H_2O	4.5×10^{-3}	
20	$(DMA)_2CHOH$+MA=leuco–MV+H_2O	4.5×10^{-3}	
21	leuco–MG+POOP=$MG^{+}PO^{-}$+POH	1.1×10^{0}	
22	leuco–CV+POOP=$CV^{+}PO^{-}$+POH	1.1×10^{0}	
23	leuco–MV+POOP=$MV^{+}PO^{-}$+POH	1.1×10^{0}	
24	POP+H_2O=2 POH	1×10^{0}	
25	POP+DMA=P–DMA+POH	1×10^{-2}	
26	B–CHO+B–CHO=B–(CO)CHOH–B	2×10^{-2}	
27	B–(CO)CHOH–B+POOP=Benzil+2 POH	1×10^{0}	

a) s^{-1}
b) Composite reaction
* Excited molecule

No. of reaction	Physical processes	Rate constant (M^{-1} s^{-1})	Notes
28	AMD–DMA*=AMD–DMA	1×10^{6}	a)
29	AMD–DMA*+DMA=AMD–DMA+DMA	1.35×10^{11}	
30	AMD–DMA*=AMD–DMA+hv	1×10^{9}	a)
31	$MG^{+}PO^{-}$+hv=$(MG^{+}PO^{-})$*	1×10^{11}	
32	$(MG^{+}PO^{-})$*=$MG^{+}PO^{-}$+hv_1	1×10^{9}	

a) s^{-1}
* Excited Molecule

Scheme of the DMA+POOP reaction



Appendix

Since ACUCHEM is a simple differential equation system solving program it works with the "trial and error" procedure. The rate-constants tabulated are the final ones which have been used to calculate the time-concentration dependence for all species included.

It should be noted that the results of the computer simulation do not prove that this is "the" mechanism of this reaction. This could be one of the possible mechanisms especially taking into account the different possible reaction pathways of the intermediates formed. The reality of the radical pathway assumed has a much higher probability since the measurement of CL is a special tool in studying directly the light emitting highly exothermic radical termination reactions.

The financial support of the Hungarian Academy of Science (OTKA 1528 and 19430) is gratefully acknowledged. Thanks are also due to Dr. Á. Keszler for performing the GC-MS measurements.

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(Received: May 5, 1997 E 9550
final version: October 10, 1997)