

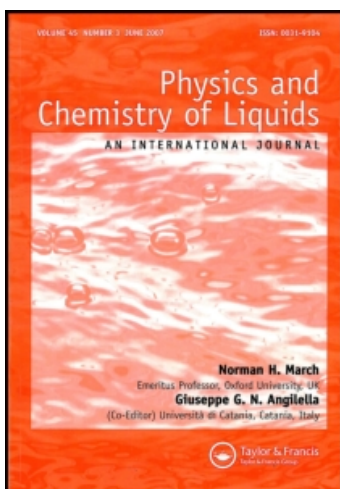
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## Physics and Chemistry of Liquids

Publication details, including instructions for authors and subscription information:

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### Studies on the Photochemical Oxidation of 1,3-Diphenylisobenzofuran and Cis-Cyclooctene in *N,N*-Dimethylformamide-Propanol Binary Mixture

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**To cite this Article** Kinart, W. J. , Kinart, C. M. , Dzikowski, T. and Thuong, Q. Tran(2004) 'Studies on the Photochemical Oxidation of 1,3-Diphenylisobenzofuran and Cis-Cyclooctene in *N,N*-Dimethylformamide-Propanol Binary Mixture', *Physics and Chemistry of Liquids*, 42: 3, 297 – 303

**To link to this Article:** DOI: 10.1080/00319100410001697314

**URL:** <http://dx.doi.org/10.1080/00319100410001697314>

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# STUDIES ON THE PHOTOCHEMICAL OXIDATION OF 1,3-DIPHENYLISOBENZOFURAN AND CIS-CYCLOOCTENE IN *N,N*-DIMETHYLFORMAMIDE–PROPANOL BINARY MIXTURE

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(Received 7 August 2003)

Kinetic studies on the photochemical oxidation of 1,3-diphenylisobenzofuran have been carried out in binary liquid mixtures of *N,N*-dimethylformamide (DMF) with 1-propanol (PrOH). The strongest influence of solvating effects upon the course of this reaction was observed for compositions of the studied mixture corresponding respectively to *ca.* 50 mol% of PrOH. Additionally, we have carried out analogous studies of photooxidation of cis-cyclooctene. Similarly as previously, the noticeable influence of solvating effects upon the course of this reaction corresponded to *ca.* 50 mol% of DMF. We suspect that the mechanism of this effect is associated with the formation of the polar intermediate during the ene reaction being easier.

*Keywords:* Kinetic studies; Photochemical oxidation; Singlet oxygen

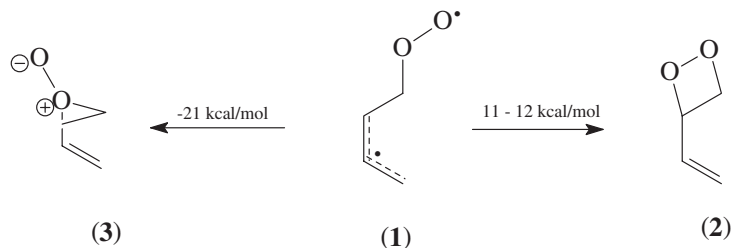
## INTRODUCTION

The Diels-Alder reaction between singlet oxygen and conjugated dienes and ene reactions of <sup>1</sup>O<sub>2</sub> with olefins are the general photochemical oxidations. The Diels-Alder reaction of singlet oxygen has found much application in synthesis, for the stereo-controlled generation of two 1,4-related oxygen bearing stereocenters. This has been exemplified by the recent synthesis of some agarofuran sesquiterpenes and in Kuwajima's total synthesis of Taxol [1].

The recent reports with reliable levels of theory have appeared and concur that the favored mechanism of this reaction with normal dienes is a stepwise one passing through diradical intermediates [2]. The diradical formed between singlet oxygen and butadiene could be close to a dioxetane (**2**), with a barrier of 1–12 kcal mol<sup>-1</sup> or to a peroxide (**3**), with a barrier of ~21 kcal mol<sup>-1</sup> (Scheme 1).

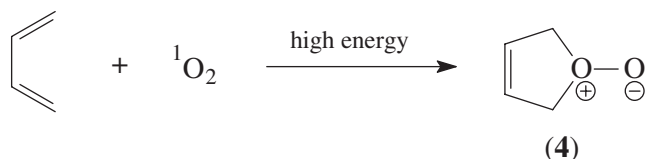
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SCHEME 1

A third mechanism was also considered by Babrowski *et al.*, involving the cheletropic addition of singlet oxygen to butadiene to form a zwitterionic peroxolane [4] (Scheme 2). This species was formed via both concerted and stepwise paths, but both were more than 10 kcal mol<sup>-1</sup> higher in energy than those already discussed.

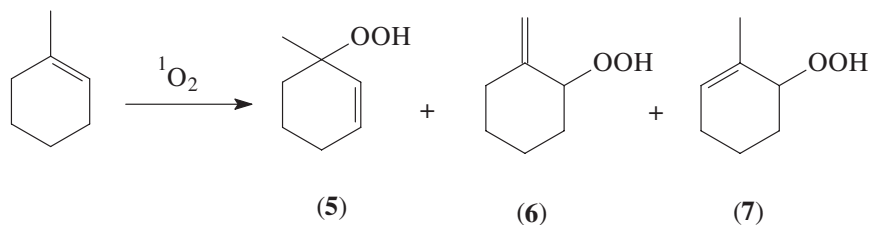


SCHEME 2

The ene reaction of singlet oxygen was discovered early in the last century [3], but the active oxidant was only identified as an excited singlet state of oxygen in the mid-60s by the groups of Foote and Corey [4]. This reaction, which is sometimes referred to as the Schenck reaction, has found applications in synthesis. These were reviewed recently by Prein and Adam [5]. The application of singlet oxygen ene reaction has been illustrated well by the recent synthesis of asteriscanolide by Paquette and co-workers [6]. Adam and co-workers have recently developed new methods for stereocontrol in these reactions [7]. There is a long history of quantum mechanical studies of this reaction [8], but only recently have methods for multiconfigurational and diradical systems approached the accuracy necessary to distinguish between the many possible mechanisms [9].

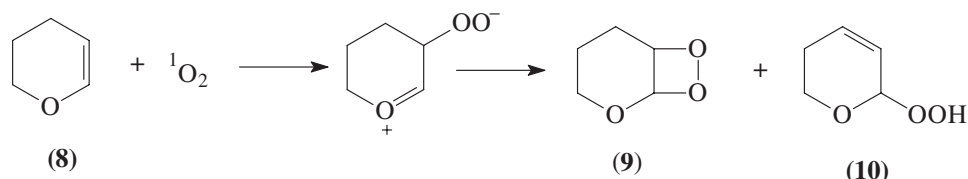
Solvent effects in photooxidation reactions have puzzled many researchers. Foote has written that for the photooxidation of 2-methyl-2-pentene in a series of solvents that “no trend in the results ( $\beta$  values) with polarity is observed...” [10]. Gollnick in his excellent review of photooxidation reactions more than once refers to the confusing effect of solvents on photooxidation reactions and the lifetimes of singlet oxygen in various solvents [11].

Courtneidge compared products of photooxidation of 1-methyl-1-cyclohexene carried in different solvents [12].

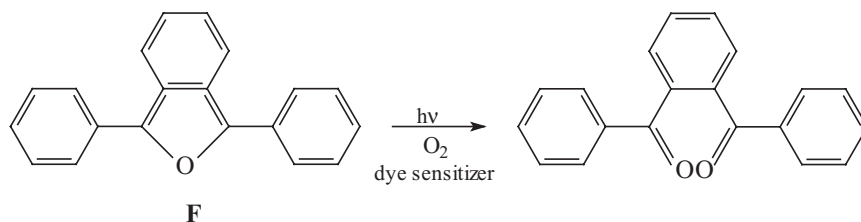


When oxidation was carried in  $\text{CH}_2\text{Cl}_2$  (using TPP as sensitizer) the ratio of hydroperoxides (5):(6):(7) was equal to 41:43:16. With increase of the polarity of the solvent, there was an observed increase of the product (5) at the expense of (6).

Frimer [13] observed that photooxidation of unsaturated ether (8) in polar solvent leads to the cycloaddition product (9), whereas in nonpolar solvent the ene product (10) is formed.



Stratakis [14] studied the influence of the solvent effect on the stereoselectivity of the reaction of  $^1\text{O}_2$  with different allyl alcohols. Also the influence of the solvent polarity on the metalloene reaction of  $^1\text{O}_2$  was studied [15].



1,3-Diphenylisobenzofuran (F) is very reactive with singlet oxygen [16]. We have measured the yield of this reaction carried in different mixtures of *N,N*-dimethylformamide (DMF) and 1-propanol (PrOH). The method involves following the disappearance of (F) by measuring the absorbance at 420 nm of samples after and before the illumination.

It is known that cis-cyclooctene undergoes ene reactions with singlet oxygen [17]. Cis-cyclooctene reacts with  $^1\text{O}_2$  to give an allylic hydroperoxide as the sole product. The aim of the present study was to compare, observed by us, the variations in yields of the reaction of the photochemical oxidation of 1,3-diphenylisobenzofuran and cis-cyclooctene carried in analogous mixtures. The concentration of 1-hydroperoxy-2-cyclooctene was determined by the amperometric titration. Previously we have investigated the internal structure of the mentioned liquid binary mixture (DMF + PrOH). We proved the formation of the complex of the DMF · PrOH type in the studied mixture [18]. Therefore, we were anxious to learn how yields of two reactions of the photochemical oxidation, differing widely in their mechanism, will be affected by properties of the mixed solvent when carried out in mixtures of DMF and PrOH.

## EXPERIMENTAL

UV-spectra were recorded on a Specord spectrometer (Carl Zeiss Jena) using 10 mm cells. A solution of cis-cyclooctene (0.846 g, 7.68 mmol) and methylene blue (10 mg)

in DMF + PrOH liquid mixtures ( $10\text{ cm}^3$ ), the composition of which was varied over the whole composition range, was vigorously stirred under oxygen while being irradiated with light from 200 W sodium lamp for 30 min. The concentration of the newly obtained hydroperoxide was determined by an amperometric titration using two platinum electrodes and  $0.1\text{ mol dm}^{-3}$  solutions of  $\text{Na}_2\text{S}_2\text{O}_3$ , which followed the addition of 1 g of KI,  $10\text{ cm}^{-3}$  of acetic anhydride and 50 mL of water to the reaction mixture. In purpose to compare obtained results using amperometric analysis with values based on chromatographic analysis, we have carried a reductive work-up using triphenylphosphine of 1-hydroperoxy-2-cyclooctene obtained by photooxidation of cyclooctene in DMF and PrOH at different irradiation times. The reaction mixture was initially separated from sensitizer by column chromatography using a mixture of ethyl acetate and petroleum ether (1/4, v/v) and then analysed by analytical HPLC (eluent 10% isopropyl alcohol in hexane). The obtained results using HPLC and amperometric analysis were identical. A solution of 1,3-diphenylisobenzofuran (20 mg, 0.073 mmol) and methylene blue (2 mg) in DMF + PrOH liquid binary mixtures ( $5\text{ cm}^3$ ) whose composition was varied over the whole composition range, was vigorously stirred under oxygen while being irradiated with light from 400 W sodium lamp for 6 min. The progress of the reaction was monitored by measuring the absorbance at 420 nm. All illuminations were carried out under the same conditions (pressure of oxygen under the solution, intensity of irradiation of the sample etc. were constant).

## RESULTS AND DISCUSSION

The yield of the reaction of the photochemical oxidation of cis-cyclooctene was measured as the function of the composition of DMF + PrOH binary mixtures (see Table I

TABLE I The yield of the reaction of the photochemical oxidation of  $0.768\text{ mol dm}^{-3}$  solution of cis-cyclooctene as a function of composition of the mixed solvent DMF + PrOH, at 298 K

DMF (mol%)	Yield of the reaction (%)
0.00	2.30
4.87	2.50
9.61	2.90
14.30	3.60
19.52	3.90
24.24	4.00
29.34	4.20
34.10	4.80
39.50	5.90
44.00	6.80
49.23	7.50
54.20	7.45
59.29	7.30
64.12	7.20
69.40	7.10
74.62	7.05
79.65	6.95
84.58	6.90
89.63	6.85
94.73	6.70
100.00	6.40

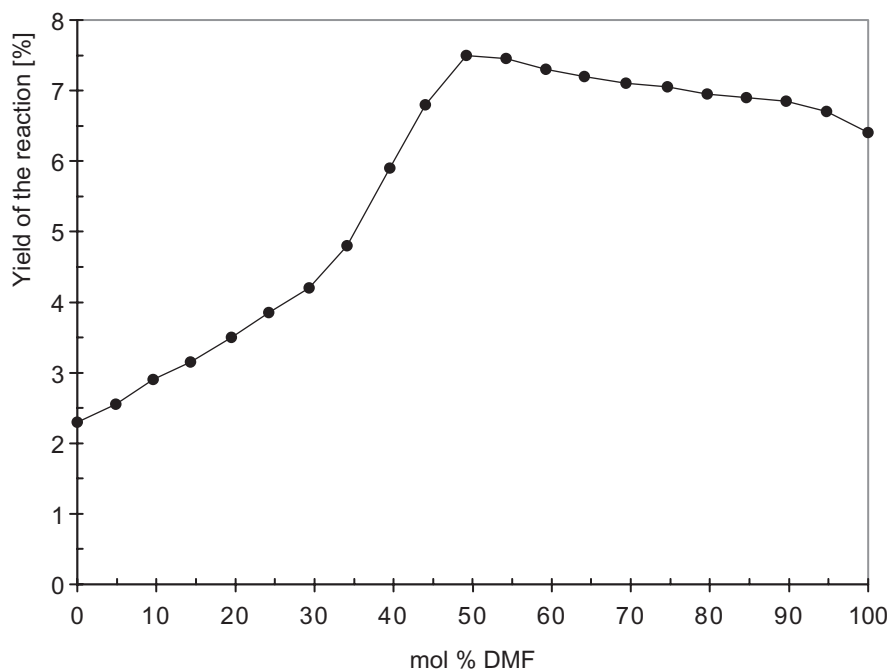


FIGURE 1 The yield of the reaction of the photochemical oxidation of  $0.768 \text{ mol dm}^{-3}$  solution of cis-cyclooctene as a function of composition of the mixed solvent DMF + PrOH, at 298 K.

and Fig. 1). It exhibits the maximum deviation from ideality for the composition corresponding to *ca.* 50 mol% of DMF (see Fig. 1). We suspect that the mechanism of this effect is associated with the formation of the polar intermediate during the ene reaction being easier. To prove this assumption we have carried out photo-oxygenations of solutions of 1,3-diphenylisobenzofuran in the same binary solvent mixture (see Table II and Fig. 2).

We have been anxious that the hydroperoxide from the reaction of singlet oxygen with cis-cyclooctene is thermally not stable, and its stability may vary with the solvent or solvent composition at a given temperature. Therefore, we have carried out blank experiments necessary to evaluate the composition of the hydroperoxide during irradiation or work-up. For example we have stored pure hydroperoxide (1-hydroperoxy-2-cyclooctene) for 30 min in DMF, PrOH and their mixtures or we have irradiated the analogous mixtures for 5, 10, 20 and 30 min with light from 200 W sodium lamp. The amperometric titration of studied samples indicated that the composition of the hydroperoxide was less than 4%. No influence of the solvent or its composition at decomposition of the hydroperoxide was observed. The yield of decrease of the concentration of the hydroperoxide was solvent independent. The analysis of the curve illustrating the changes of the yield of the reaction of the photochemical oxidation of 1,3-diphenylisobenzofuran as a function of the composition of the binary liquid mixture displays the decrease in the region close to 50 mol% of DMF (see Fig. 2). It has been shown by other authors that the above reaction is solvent sensitive [16]. The  $\beta$  values (the ratio of the rate of decay of singlet oxygen ( $k_d$ ) and the rate of the reaction of  $^1\text{O}_2$  ( $k_{rx}$ ) with 1,3-diphenylisobenzofuran) have usually been measured.

TABLE II The yield of the reaction of the photochemical oxidation of  $1.48 \cdot 10^{-2} \text{ mol dm}^{-3}$  solution of 1,3-diphenylisobenzofuran as a function of composition of the mixed solvent DMF + PrOH, at 298 K

DMF (mol%)	Yield of the reaction (%)
0.00	100.0
4.87	97.0
9.61	95.0
14.30	94.5
19.52	94.0
24.24	93.5
29.34	93.5
34.10	92.5
39.50	92.0
44.00	92.0
49.23	90.0
54.20	88.0
59.29	85.0
64.12	81.0
69.40	77.0
74.62	72.5
79.65	68.0
84.58	64.0
89.63	61.0
94.73	59.0
100.00	58.0

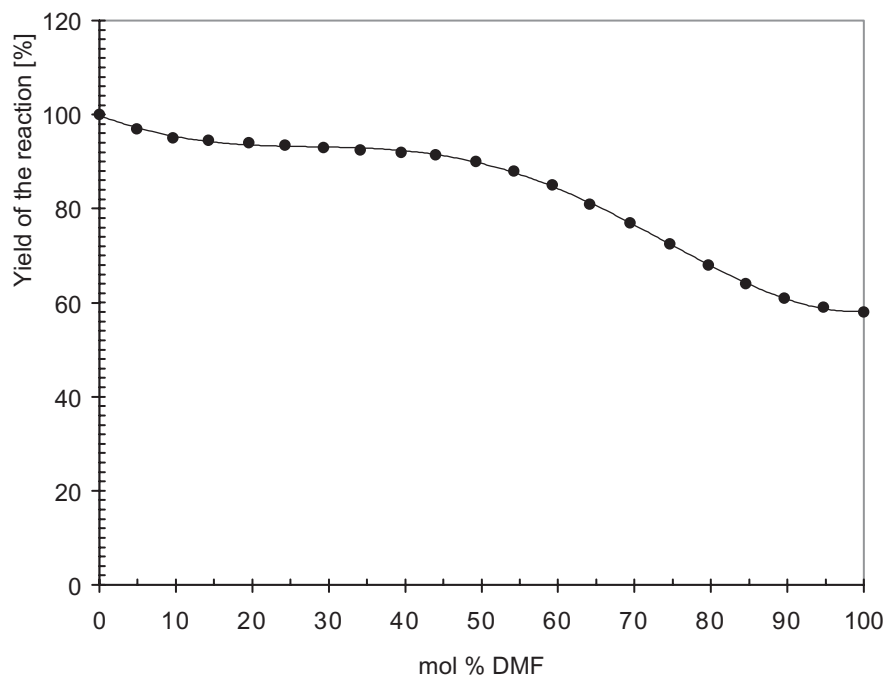


FIGURE 2 The yield of the reaction of the photochemical oxidation of  $1.48 \cdot 10^{-2} \text{ mol dm}^{-3}$  solution of 1,3-diphenylisobenzofuran as a function of composition of the mixed solvent DMF + PrOH, at 298 K.

Therefore, assuming that the yield of this reaction reflects in a quantitative way changes in  $\beta$  value, we expect that the catalytic influence of the mixed solvent at the composition corresponding to *ca.* 50 mol% of DMF in the case of photooxygenation of *cis*-cyclooctene cannot be explained by possible variations in the concentration of  $^1\text{O}_2$  under heterogeneous conditions, of  $^1\text{O}_2$ , or of its lifetime. Otherwise the increase of the yield of the reaction of photooxygenation of (F) should be observed here. We suspect that the mechanism of this effect is associated with the formation of the polar intermediate during the ene reaction being easier. Previously we have investigated the internal structure of the liquid binary mixture of DMF and PrOH by comparing its  $^1\text{H-NMR}$  spectral characteristics with the corresponding macroscopic properties such as relative permittivity, density, viscosity and calculated from these data molar volumes and kinematic viscosity [18]. They show the greatest deviations from ideality at the composition equal to *ca.* 50 mol% of DMF, which corresponds to the formation of the complex of the DMF · PrOH type in the studied mixture.

We realize that the precise analysis of measured yields of studied reaction may suffer from some limitations due to variations of lifetime of singlet oxygen and its rate constant of reaction as a function of some parameters. Variations in these individual rate constants can be hidden if only mentioned yields are measured. Moreover, the observed effects may be associated with deactivation of singlet oxygen by the solvent as well as by sensitizer whose activity is pH dependent. Therefore, the complete explanation of the influence of the internal structure and properties of solvent on the rate of the studied reactions will require further studies.

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