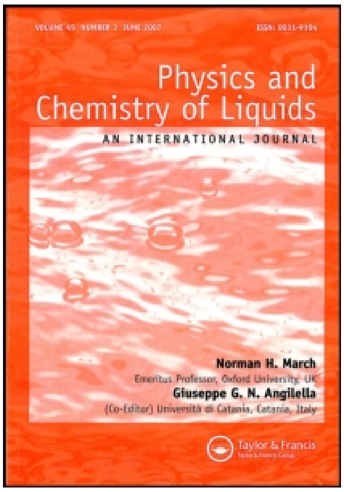

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Studies On the Photochemical Oxidation of *Cis*-Cyclooctene and the Addition of Diallyldibutyltin to Diethyl Azodicarboxylate in Mixtures of *N,N*-Dimethyl-Formamide and Dimethyl Sulfoxide

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To cite this Article Kinart, Cezary M. , Romanowski, StanisŁaw J. , Kinart, Wojciech J. , Śnieć, Ewa and Tylak, Izabela(1999) 'Studies On the Photochemical Oxidation of *Cis*-Cyclooctene and the Addition of Diallyldibutyltin to Diethyl Azodicarboxylate in Mixtures of *N,N*-Dimethyl-Formamide and Dimethyl Sulfoxide', Physics and Chemistry of Liquids, 37: 5, 521 — 528

To link to this Article: DOI: 10.1080/00319109908035935

URL: http://dx.doi.org/10.1080/00319109908035935

Phys. Chem. Liq., 1999, Vol. 37, pp. 521-528
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STUDIES ON THE PHOTOCHEMICAL OXIDATION OF *CIS*-CYCLOOCTENE AND THE ADDITION OF DIALLYLDIBUTYLTIN TO DIETHYL AZODICARBOXYLATE IN MIXTURES OF *N,N*-DIMETHYLFORMAMIDE AND DIMETHYL SULFOXIDE

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(Received 15 January 1998)

Kinetic studies of the photochemical oxidation of *cis*-cyclooctene and the addition of diallyldibutyltin to diethyl azodicarboxylate have been carried out in binary liquid mixtures of *N,N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO). The strongest influence of solvating effects for the course of both reactions was observed for composition corresponding to ca. 50 mol.% of DMF. We believe that the intermolecular association leading to formation of DMSO • DMF type complexes is responsible for this property. The optimization of the geometry, energy and hydrogen bond lengths of DMSO • DMF dimers calculated by means of the semiempirical quantum chemical method proved their stability.

Keywords: Kinetic studies; photochemical oxidation; hydrogen bond

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INTRODUCTION

The present work is a continuation of series of studies on analysis of intermolecular interactions and internal structures of some liquid binary mixtures, in which dimethyl sulfoxide (DMSO) or *N,N*-dimethylformamide (DMF) is one of two constituents [1–4]. We attempted in this work to gain some new information regarding intermolecular interactions between components of liquid mixtures DMSO–DMF. De Visser and Somsen [5] on the base of the analysis of changes of densities, molar volumes, partial molar volumes and molar heat capacities as a function of the mole fraction of DMF assumed that the mixture DMSO–DMF can be regarded as almost ideal with lack of intermolecular interactions. The opposite view was expressed in the work of Jonin *et al.*'s [6] and in our recent work [7]. In this paper [7], using the ^{1}H-NMR examinations of liquid DMSO–DMF binary mixtures and changes in their main physicochemical properties, the possibility of formation of stable DMSO • DMF type complexes was suggested. Previously, Young reported a regular solvent effect on the rate of the reaction of singlet oxygen with β-carotene [8]. In this work we attempted to find further evidences supporting this view by analysing kinetic data of photochemical oxidation of *cis*-cyclooctene and the addition of diethyl azodicarboxylate to diallyldibutyltin in the binary liquid mixtures of DMSO with DMF. The semiempirical quantum chemical calculations (MOPAC package) methods were applied to optimize the geometry, binding energy and hydrogen-bond lengths of dimers formed by molecules of dimethyl sulfoxide and *N,N*-dimethylformamide.

EXPERIMENTAL

N,N-Dimethylformamide and dimethyl sulfoxide (Aldrich) were stored over 4 Å molecular sieves of for at least 48 h and distilled twice under reduced pressure. Diallyldibutyltin was prepared according to known procedure [9]. The example mixture for photooxidation was prepared as follows: (1) 1.7 mol·dm^{-3} solution of $LiClO_4$ (5.5 cm^{-3}) containing 0.423 g of *cis*-cyclooctene and 10 mg of methylene blue was irradiated by 30 minutes using sodium lamp. Concentration of

1-hydroperoxy-2-cyclooctene was determined by amperometric titration with $Na_2S_2O_3$ using two platinum electrodes. (2) 101 mg (0.32 mmol) of diallyldibutyltin was added to 1 cm^3 of 1 mol·dm^{-3} solution of $LiClO_4$ containing 55.3 mg (0.317 mmol) of diethyl azodicarboxylate. The reaction was followed visually by fading of the color of the azo compound. *N*-allyl-*N*′-tributylstannylhydrazodicarboxylate obtained as the product of the reaction. Isolation of the product by gradient chromatography (30% ethyl acetate-petroleum ether) gave diethyl *N*-allylhydrazodicarboxylate as an oil.

RESULTS AND DISCUSSION

The yield of the reaction of the photochemical oxidation of *cis*-cyclooctene in the pure solvent and in 1.7 M solutions of $LiClO_4$ was measured as a function of the composition of binary mixture (DMSO–DMF). We have also measured time of the reaction for the addition of diallyldibutyltin to diethyl azodicarboxylate in 1 M solutions of $LiClO_4$ in analogous mixtures. The NMR spectra of products from the above two reactions have been described in the literature, and provided the basis of the identifications reported in this work [10, 11]. Previously, we have shown the catalytic effect of $LiClO_4$ on the allyl-hydrogen and allyl-tin enes with azo compounds and singlet oxygen as enophiles [11, 12]. All these data have been collected in Tables I and II and are visualized at Figures 1 and 2.

TABLE I The yield of the reaction of the photochemical oxidation of *cis*-cyclooctene as a function of composition of the mixed solvent DMSO–DMF

% mol. DMSO	*Yield of reaction%*	
	1.7 mol·dm^{-3} $LiClO_4$	*Pure solvent*
0	2.5	1.3
10.78	5.8	3.05
21.37	6.9	3.9
31.77	7.3	3.9
42.02	7.3	4.2
52.08	7.6	4.8
61.98	9.3	6.0
71.71	10.3	6.7
81.30	10.6	6.9
90.73	10.9	7.0
100	11.1	7.1

TABLE II Time of the reaction for the addition of diallyldibutyltin to diethyl azodicarboxylate at 298 K in DMSO–DMF binary mixtures

% mol. DMSO	*Time of the reaction hours* 1 *mol·dm*$^{-3}$ *LiClO*$_4$
0	24.5
10.78	22.0
21.37	20.0
31.77	18.5
42.02	17.0
52.08	16.5
61.98	17.0
71.71	17.5
81.30	18.5
90.73	20.0
100	21.5

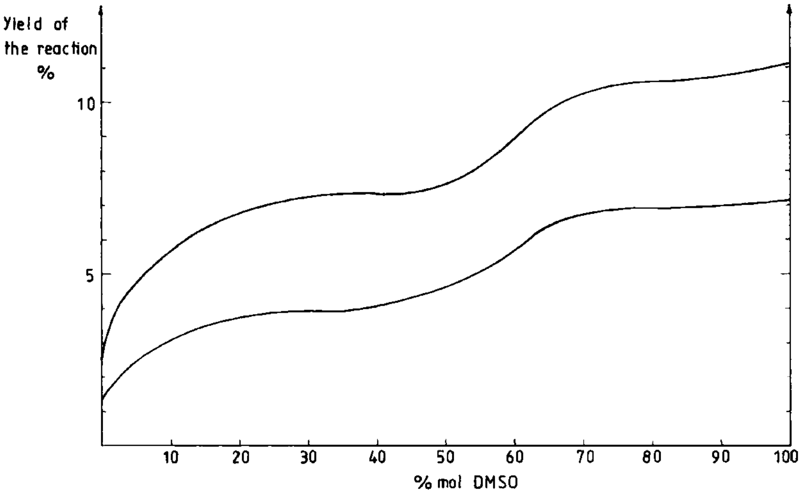

FIGURE 1 Changes in the yield of the reaction of the photochemical oxidation of *cis*-cyclooctene as a function of composition for the liquid DMSO–DMF mixture, at 298 K.

The rapid increase of the yield of the reaction with the gradual addition of DMSO to DMF up to 10 mol.% of DMSO corresponds to the composition where according to other authors [6] a destruction of the DMF structure by molecules of DMSO is observed. The region of the composition corresponding to ca. 50 mol.% of DMF is also very interesting from the point of view of the characteristic deviation from the linearity of the curve representing the yield of the reaction as a function of the composition. We believe that the intermolecular

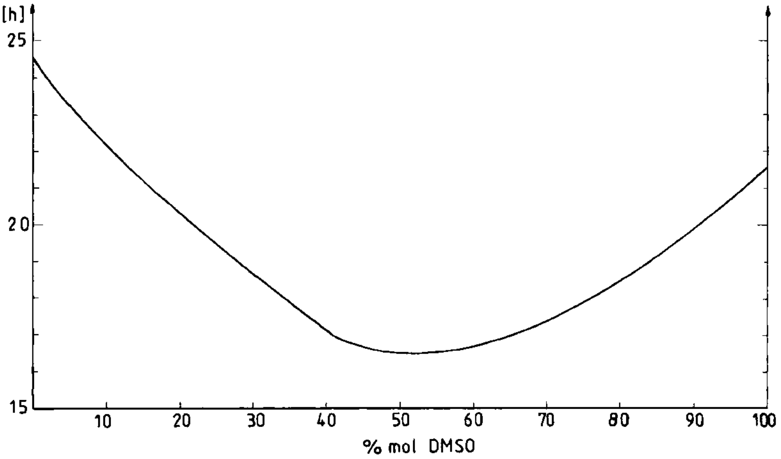

FIGURE 2 Changes in the time of the reaction for the addition of diallyldibutyltin to diethyl azodicarboxylate as a function of composition for the liquid DMSO–DMF mixture, at 298 K.

association leading to formation of DMSO • DMF type complexes is responsible for this feature. Also so it can be seen in Figure 2, that time of the reaction for the addition of diallyldibutyltin to diethyl azodicarboxylate in 1 M solutions of $LiClO_4$ exhibits minimum at this composition.

We have applied quantum chemical calculations (MOPAC 6.0) [13, 14] for the purpose of designating the spatial structure of intermolecular "complexes" of the DMSO • DMF type and calculation of the strength of the hydrogen bonds formed between molecules of DMSO and DMF. All steps of calculations were analogous to these described in our previous papers on semiempirical quantum chemical studies on the structure and interactions of clusters formed in formamide–1-propanol [15], dimethyl sulfoxide–methanol [2] and *N*,*N*-dimethylformamide–ethanol [16] liquid mixtures. In the first step of the calculation the enthalpy of formation and dipole moments of the fully optimized DMF and DMSO single molecules have been computed by means of AM1 and PM3 and compared with experimental results. The values obtained have been published in our previous papers [2, 16]. From the analysis of the results described above for single DMF and DMSO molecules the PM3 method was chosen for cluster calculations. Thus, in the second step the DMSO–DMF (dimer) geometries were determined. In this case the optimized geometries of separate DMF and DMSO molecules were kept frozen and only intermolecular distances and angles were optimized. A choice of DMSO–DMF clusters for calculations follows from the earlier hypothesis based on the experimental data, that the most stable intermolecular 'complexes' are formed at ca. 50 mol.% DMF in DMSO–DMF mixtures [7].

The optimized clusters geometries of the dimer are illustrated in Figure 3 and the main parameters for the hydrogen bonds of two clusters are listed in Table III.

The hydrogen-bond strengths ΔE^{H} in Table III were determined as a cluster interaction energy calculated per hydrogen bond, *i.e.*, according the equation:

$$\Delta E^{\mathrm{H}} = \left[E_{\mathrm{Cl}}^{\mathrm{PM3}} - \left(E_{\mathrm{DMSO}}^{\mathrm{PM3}} + E_{\mathrm{DMF}}^{\mathrm{PM3}}\right)\right] \Big/ n,$$

where n is the number of hydrogen bonds in the DMSO–DMF cluster. It follows from Table III that the hydrogen-bond strength in the DMSO–DMF cluster, *i.e.*, $\Delta E^{\mathrm{H}} = -21.35\,\mathrm{kJ{\cdot}mol^{-1}}$ is almost twice as high as O···H hydrogen-bond strength calculated for nitromethane thiourea clusters [17] ($\Delta E^{\mathrm{H}} = -9.93$ to $-13.78\,\mathrm{kJ{\cdot}mol^{-1}}$ with bond

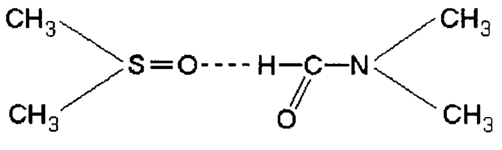

FIGURE 3 Geometrical structure of the DMSO–DMF dimer optimized by the PM3 method.

TABLE III Characteristics of the hydrogen O···H type bonds and charge transfer in DMSO–DMF clusters calculated by means of PM3

DMSO–DMF (dimer)	*number of hydrogen bonds, n*	$r_{O\cdots H}$ [Å]	ΔE^{H} [$kJ\cdot mol^{-1}$]	Δq_i
	1	1.80	21.35	DMSO, 0.022 DMF, −0.022

lengths $r = 2.17-2.31$ Å respectively) and is comparable with the strength in thiourea–ethanol trimers [18] ($\Delta E^{\mathrm{H}} = -29.79\,\mathrm{kJ{\cdot}mol^{-1}}$ with $r = 1.62$ Å). Recently the O $\cdots$ H hydrogen strength was calculated for formamide–1-propanol (F–PrOH) [15] ($\Delta E^{\mathrm{H}} = -13.07$ and $-11.57\,\mathrm{kJ{\cdot}mol^{-1}}$ with average $r = 2.17$ Å for 2 F–PrOH trimer and 3 F–2PrOH pentamer, respectively) as well as for *N*,*N*-dimethylformamide–ethanol (DMF–EtOH) [16] ($\Delta E^{\mathrm{H}} = -13.04\,\mathrm{kJ{\cdot}mol^{-1}}$ with $r = 1.81$ Å for DMF–EtOH dimer) and for dimethyl sulfoxide–methanol (DMSO–MeOH) [2]. ($\Delta E^{\mathrm{H}} = -22.77$ and $-22.52\,\mathrm{kJ{\cdot}mol^{-1}}$ with average $r = 1.79$ Å for DMSO–MeOH dimer and DMSO–2 MeOH trimer, respectively). The stable dimer shown in Figure 3 seems to be responsible for the deviations from linearity of the yield of the reaction of photochemical oxidation of *cis*-cyclooctene and the minimum of time of the reaction for addition of diallyldibutyltin to diethyl azodicarboxylate at ca. 50 mol.% of DMF in the mixture. This assumption follows from the fact that strong charge transfer from DMSO to DMF takes place in the dimer, as it can be seen in the last column of Table III. The dimer as a whole can be treated as a dipole with strong poles generating the high average dipole moment μ. There is a good evidence from stereochemical and that hydrogen isotope studies that hydrogen-ene reaction and metalloene-reaction proceed through an intermediate ene-enophile complex, which then undergoes internal hydrogen transfer [19]. Previously, we have shown that reactions of this type were catalysed by $\mathrm{LiClO_4}$ [11, 12]. Present results seem to indicate that one may expect also the influence of solvent effects on the course of studied ene reactions. However, the explanation of the influence of dipoles of mixed solvent on a mechanism of ene-reactions will require further studies. It seems also worth mentioning that no considerable difference of the course of the yield of reaction *vs.* composition of the mixed solvent was observed for the photochemical oxidation of *cis*-cyclooctene in pure mixtures and 1.7 M solutions of $\mathrm{LiClO_4}$.

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