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Solvent Effect on Photoisomerisation of 3-Methyl-1-phenylbutane-1,2-dione 2-Oxime

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Photoisomerisation of (2*E*)- and (2*Z*)-3-methyl-1-phenylbutane-1,2-dione 2-oxime (MPBDO) in several solvents was studied. With increasing dielectric constants of solvents, kinetic constants of forward reactions (*E*-form→*Z*-form) did not change appreciably but those of reverse reactions (*Z*-form→*E*-form) decreased. The positive correlation was found between equilibrium constants of photoisomerisation and dielectric constants of solvents.

Key words photoisomerisation; oxime; solvent effect; dielectric constant; equilibrium constant

It is well known that the compounds having C=C, N=N or C=N bond isomerise readily by light. Many reports on the isomerisation of the oximes and their derivatives which have C=N bond are published,[1—4] however, there are few papers on the photochemical studies of α-oxo-oximes.[5]

In the present paper, the kinetic study of photoisomerisation of 3-methyl-1-phenylbutane-1,2-dione 2-oxime (MPBDO) in several solvents is reported (Chart 1).

Experimental

Materials 3-Methyl-1-phenylbutane-1-one (TOKYO KASEI KOGYO Co. LTD.) and *tert*-butyl nitrite (ACROS ORGANICS) were purified by distillation prior to use. All solvents using photochemical reactions were HPLC or spectroscopy grade obtained from KANTO CHEMICAL Co. INC.

Synthesis of MPBDO *E*- and *Z*-MPBDO were prepared by nitrosation of 3-methyl-1-phenylbutane-1-one with *tert*-butyl nitrite in the presence of hydrogen chloride by use of a similar procedure as described by Hartung and Crossley for the synthesis of isonitrosopropiophenone.[6] A mixture of *E*- and *Z*-MPBDO (32.7 g) was obtained in 29% yield from 96.7 g of 3-methyl-1-phenylbutane-1-one. The resulting mixture was separated by HPLC.

Separation of Resulting Mixture by HPLC HPLC was performed on JASCO PU-986/987 intelligent prep. pump and JASCO UVIDEC-100-III UV spectrophotometer connected to a System Instruments Chromatocorder 11 integrator. Merck Lichrosorb Si60 (7 μm) (25 mm×250 mm, pre-packed) column was used for HPLC analysis. As a mobile phase, ethyl acetate (25% (v/v)) and hexane (75% (v/v)) were used. *E*- and *Z*-MPBDO were obtained from the resulting mixture at the ratio of 6 to 4.

Photoisomerisation of MPBDO A solution of 1×10^{-3} mol/l of *E*- or *Z*-MPBDO was irradiated with a UVL-100HA high pressure (100 W) mercury lamp equipped with water-cooling tube (Pyrex) or a UVL-32LB low pressure (32 W) mercury lamp equipped with air-cooling tube (quartz) (RIKO-KAGAKU SANGYO Co., LTD.) at a distance of 17 cm from a reaction vessel (Pyrex). The temparature of the reaction vessel and the mercury lamp was maintained at 300 K in the same thermostat during irradiation. The reaction was followed by analysing the ratio *Z*/*E* using HPLC every 30 min. HPLC was performed on Waters-600E-MSDS equipped with Waters 484 tunable absorbance detector connected to a System Instruments Chromatocorder 11 integrator. Merck Lichrosphere Si60 (5 μm) (4 mm×250 mm, pre-packed) column and ethyl acetate (25% (v/v)) and hexane (75% (v/v)) as a mobile phase were used for HPLC analysis.

Computational Procedure The *ab initio* MO calculations were carried out with the Gaussian 98 program.[7] All of the geometry optimization and energy calculation of an isomer in a solvent were carried out using an Onsager reaction field model.[8] The optimized geometries of each isomer were determined with HF/6-31G. The electron correlation energy was corrected by the second-order Moeller-Plesset (MP2) perturbation method.

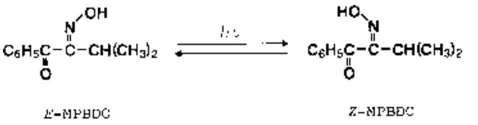

Chart 1

Results and Discussion

For the purpose of elucidation of the mechanism of photoisomerisation of α-oxo-oximes, the investigation of solvent effects on the isomerisation of *E*- and *Z*-MPBDO in several solvents was first carried out until the photostationary state (PSS) was attained. The irradiation was made repeatedly three times in the same kind of solvent. The time of attainment to the PSS was *ca.* 3—4 h.

According to the reaction procedure as described above, the concentrations of *E*- and *Z*-MPBDO were determined at regular intervals. The equilibrium constant (*K*) of the isomerisation shown in Chart 1 is expressed by Eq. 1 as follows,

$$K=[Z]_{\mathrm{PSS}}/[E]_{\mathrm{PSS}}=k/k' \qquad (1)$$

in which $[E]_{\mathrm{PSS}}$, $[Z]_{\mathrm{PSS}}$, k and k' are the concentration of *E*- and *Z*-MPBDO at PSS, the kinetic constant of forward reaction and that of reverse reaction, respectively. The summation of kinetic constants ($k+k'$) at regular intervals is calculated by Eq. 2 as follows,

$$\ln([\mathrm{A}]-[\mathrm{A}]_{\mathrm{PSS}})=-(k+k')t+\ln([\mathrm{A}]_0-[\mathrm{A}]_{\mathrm{PSS}}) \qquad (2)$$

in which $[\mathrm{A}]$, $[\mathrm{A}]_{\mathrm{PSS}}$ and $[\mathrm{A}]_0$ are the concentration of starting isomer (*E*- or *Z*-MPBDO) at the time t, that at PSS and the initial concentration of starting isomer, respectively. K was determined using $[E]_{\mathrm{PSS}}$ and $[Z]_{\mathrm{PSS}}$. And the average of ($k+k'$) at regular intervals was calculated, and then, k and k' were calculated using Eqs. 1 and 2. The dielectric constant (ε) of each solvent at 298 K from some literatures,[9,10] k, k' and K of photoisomerisation of MPBDO in each solvent are shown in Table 1. With increasing dielectric constants of solvent, k did not change appreciably but k' was liable to decrease. Using amides or alcohols as a reaction solvent, the value of K is larger than that using the other solvent. As shown in Fig. 1, the equilibrium constant K shows a linear relation with the dielectric constant ε, and the correlation coefficient is 0.920.[11] The value of K increases linearly with an increase of that of ε.

When the same experiments as described above were carried out using the low pressure mercury lamp, the rate of photoisomerisation was quite slower than that using high pressure mercury lamp and the time for attainment of PSS

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Table 1. ε of Solvent at 298 K, k, k' and K of Photoisomerisation of MPBDO in Each Solvent at 300 K

Solvent	ε	k (h^{-1})	k' (h^{-1})	K
1,4-Dioxane	2.210	0.549	1.090	0.504
Benzene	2.270	0.476	0.966	0.493
Toluene	2.380	0.379	0.829	0.458
Diethyl ether	4.200	0.469	1.100	0.432
Diisopropyl ether	4.490	0.469	1.130	0.414
tert-Butyl methyl ether	4.500	0.495	1.120	0.440
Ethyl acetate	6.020	0.390	0.852	0.458
Tetrahydrofuran	7.580	0.486	1.070	0.457
2-Butanol	16.56	0.386	0.669	0.576
1-Butanol	17.51	0.558	0.975	0.572
2-Propanol	19.92	0.502	0.815	0.617
1-Propanol	20.45	0.453	0.781	0.580
Ethanol	24.55	0.523	0.880	0.593
Methanol	32.66	0.400	0.627	0.639
N,*N*-Dimethylformamide	36.71	0.459	0.597	0.771
N,*N*-Dimethylacetamide	37.78	0.462	0.509	0.908

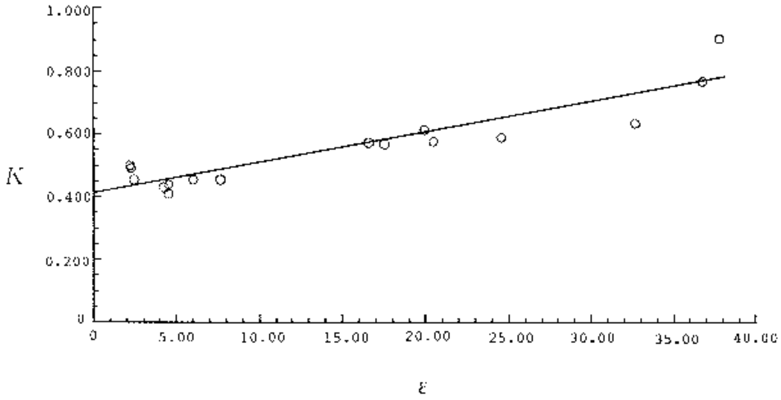

Fig. 1. Relationship between K and ε

Table 2. ε of Solvent at 298 K, E_{total} of Both Isomers and ΔE

	Diethyl ether	1-Butanol	*N*,*N*-Dimethylformamide
ε	4.20	17.51	36.71
E_{total} of *E*-MPBDO (a.u.)	−629.297313	−629.297621	−629.297688
E_{total} of *Z*-MPBDO (a.u.)	−629.296699	−629.297066	−629.297140
ΔE (kJ/mol)	1.61	1.46	1.44

was *ca.* 50—60 h. The low pressure mercury lamp emits mainly a UV ray of 254 nm, while the high pressure mercury lamp emits mainly a UV ray of 365 nm. According to some reports,[5,12)] the wavelengths emitted from a low pressure mercury lamp corresponds to π–π^* absorption band of α-oxo-oximes and those emitted from a high pressure mercury lamp corresponds to n–π^* absorption one. Thus, n–π^* absorption of MPBDO may be closely related to this photoisomerisation.

As a preliminary theoretical study on these experimental results, the thermodynamic stabilities on ground state of *E*- and *Z*-MPBDO in the three kinds of solvents (diethyl ether, 1-butanol and *N*,*N*-dimethylformamide) were investigated using *ab initio* MO calculation. The MO calculation in the presence of a solvent was performed using an Onsager reaction field model.[8)] Based on the optimised geometries of *E*- and *Z*-MPBDO in each solvent, the total energies (E_{total}) of both isomers and the difference (ΔE) in E_{total} between both isomers were calculated as shown in Table 2. With increasing dielectric constants of solvents, ΔE tends to decrease. It is considered that these calculation results support the experimental results (the value of K in a solvent with high ε is larger than that in a solvent with low ε).

The detailed investigation on the mechanisms of this reaction using *ab initio* MO calculation will be reported in the near future.

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