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1,3-Dipolar addition of nitrile ylide to olefins using the laser flash photolysis of 3-(biphenyl-4-yl)-2H-azirine

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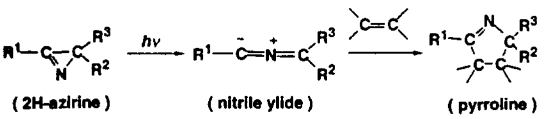
Abstract

The 1,3-dipolar addition of a nitrile ylide (NY) to various olefins (using the laser flash photolysis of 3-(biphenyl-4-yl)-2H-azirine (AZ) to generate NY) was studied as a function of the solvent polarity and temperature. A transient absorption band of NY was observed at 410 nm and the decay was enhanced on addition of a dipolarophile. The bimolecular rate constant of 1,3-dipolar addition (k_{obs}) increased with increasing ionization potential (IP) of the dipolarophile, and the k_{obs} value in cyclohexane (c-Hex) was found to be 1.2–1.5 times larger than that in acetonitrile (MeCN). The k_{obs} value of dimethyl fumarate (DF) was dependent on the solvent polarity, providing a minimum k_{obs} value at a dielectric constant ϵ of 3–7. Arrhenius plots of k_{obs} for DF gave negative activation energies in c-Hex and MeCN. These results suggest that the reaction proceeds via a complex of DF and NY. The activation energies for adduct formation and dissociation from the complex were dependent on the solvent polarity. The solvent effect is discussed in terms of the stabilization energies on solvation of NY, the complex and the adduct.

Keywords: Nitrile ylide; 1,3-Dipolar addition; Reactive intermediate; Laser flash photolysis; Solvent effect

1. Introduction

Nitrile ylides (NYs) are typical 1,3-dipoles, which have been used to synthesize heterocyclic compounds [1,2]. NY can be generated by the photolysis of 2H-azirine, and its reactivity, via 1,3-dipolar addition, has been investigated with a wide variety of dipolarophiles, such as olefins, ketones and esters (Eq. (1)) [3–7].



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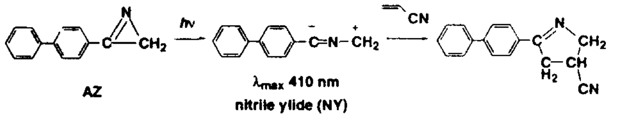
Padwa et al. [7] suggested that the 1,3-dipolar addition proceeds via a complex of NY and olefin. Kinetic studies have indicated that a complex is formed between NY and a dipolarophile as shown in Eq. (2)

$$\text{nitrile ylide} + \text{olefin} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{complex} \xrightarrow{k_2} \text{adduct} \qquad (2)$$

where k_1, k_{-1} and k_2 are the reaction rate constants of the formation of the complex, the dissociation into NY and olefin and the formation of the adduct respectively. On the basis of these reactions, the observed rate constant for the decay of NY (k_{obs}) can be written as

$$k_{obs} = k_1 k_2 / (k_{-1} + k_2) \qquad (3)$$

Recently, we have detected NY (R^1 = biphenyl-4-yl, $R^2 = R^3 = H$) by the laser flash photolysis (308 nm) of 3-(biphenyl-4-yl)-2H-azirine (AZ) [8,9]. A transient absorption with a maximum at 410 nm was observed and decayed with a rate constant of 80 s^{-1}. The transient absorption was efficiently quenched by acrylonitrile (AN). Steady state photoirradiation at 313 nm in the presence of AN gave the corresponding 1-pyrroline in good yield (90%, isolated). These results indicate that the transient species is NY with a dipole structure as shown in Eq. (4).



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Many addition reactions of NYs towards dipolarophiles, such as phenylazide [10], methyldiazoacetate [11], dimethyl diazomalonate [11], diazo(phenylsulphonyl)-acetate [11], etc., have been reported. In these reactions, a correlation between the rate constant (k) and the highest occupied molecular orbital (HOMO) or lowest unoccupied molecular orbital (LUMO) energy levels of the dipole and dipolarophile was suggested. The reactivity of NYs was analysed by the Sustmann plot [10], and the reaction was found to involve an interaction between the NY LUMO and the dipolarophile HOMO. We observed a similar dependence of the reactivity of NY on the electronic properties of carbonyl compounds; k increased with an increase in the ionization potential (IP) due to carbonyl π electrons [12]. In this paper, the reactivity of NY towards various olefins was studied.

2. Results

2.1. Reaction towards various types of olefin

The reaction of various types of olefin with NY (using the laser flash photolysis of AZ to generate NY) was carried out in cyclohexane (c-Hex) and acetonitrile (MeCN) as typical non-polar and polar solvents respectively. On laser irradiation of AZ, the transient absorption band of NY with a maximum at 410 nm was observed together with an intense T_1–T_n absorption of AZ around 410 nm [8,9]. In order to quench the triplet state of AZ, all sample solutions were saturated with oxygen. Thus laser flash photolysis resulted in the selective formation of NY with an absorption maximum at 410 nm.

The decay profiles of NY followed pseudo-first-order kinetics in the presence of olefins. The bimolecular rate constants of 1,3-dipolar addition (k_{obs}) were determined for a series of olefins and are summarized in Table 1.

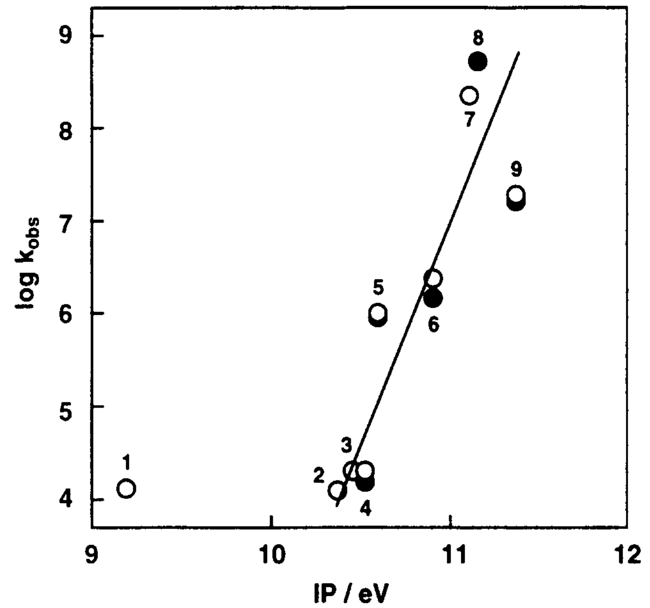

Fig. 1. Relationship between logk_{obs} for the reaction of NY with a series of olefins and the ionization potential (IP) of the olefins: 1, vinyl acetate; 2, methacrylonitrile; 3, styrene; 4, methyl methacrylate; 5, methyl acrylate; 6, acrylonitrile; 7, dimethyl fumarate; 8, fumaronitrile; 9, dimethyl acetylene-dicarboxylate. Each rate constant (k_{obs}) was determined from the laser flash photolysis (308 nm, 15 ns, 100 or 70 mJ per pulse) of AZ with olefins in cyclohexane (○) and acetonitrile (●) under oxygen at room temperature.

The logarithm of k_{obs} was plotted vs. IP of the olefins [13–16] as shown in Fig. 1. For electron-deficient olefins, linear relationships were observed in both solvents. Two characteristic features of these results are as follows: (1) k_{obs} increases with an increase in IP in both solvents; (2) k_{obs} is approximately 1.2–1.5 times larger in c-Hex than in MeCN. In contrast, for electron-rich olefins, such as butyl vinyl ether (IP = 9.08 eV [17]), 2,3-dimethyl-2-butene (8.30 eV [18]), 1,4-dioxene and 1-(1-cyclohexenyl)-pyrrolidine (7.40 eV [15]), the decay rates of NY are not dependent on

Table 1
Reaction rate constants of NY with olefins

Compound		IP (eV)	k_{obs} (M^{-1} s^{-1})	
			In c-Hex	in MeCN
Fumaronitrile	(FCN)	11.16	–	5.1×10^8
Dimethyl fumarate	(DF)	11.11	2.2×10^8	–
Dimethyl acetylene-dicarboxylate	(MAC)	11.37	1.9×10^7	1.6×10^7
Acrylonitrile	(AN)	10.91	2.3×10^6	1.4×10^6
Methyl acrylate	(MA)	10.60	9.8×10^5	9.1×10^5
Methyl methacrylate	(MMA)	10.53	2.0×10^4	1.5×10^4
Methacrylonitrile	(MAN)	10.37	1.2×10^4	–
Styrene	(St)	10.45	2.0×10^4	–
Vinyl acetate	(VAc)	9.19	1.3×10^4	–
Butyl vinyl ether	(BVE)	9.20	[a]	–
2,3-Dimethyl-2-butene	(DB)	8.40	[a]	–
1,4-Dioxene	(DO)	–	[a]	–
1-(1-Cyclohexenyl)-pyrrolidine	(CP)	7.40	[b]	–

[a] Decay of NY could not be measured.

[b] AZ reacted before irradiation.

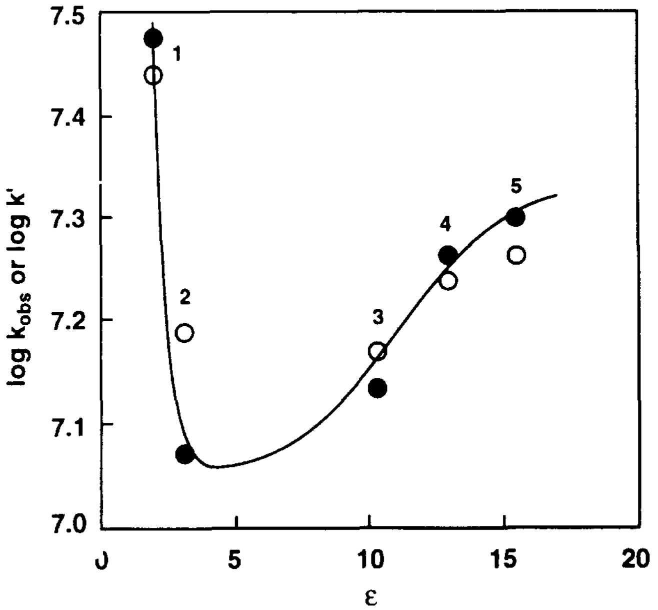

Fig. 2. Solvent polarity effect on the reaction of NY with dimethyl fumarate; the rate constants observed in a series of solvents (k_{obs}, ○) and the viscosity-corrected rate constants ($k' = (\eta/9\times10^{-4})k_{obs}$, ●) are plotted vs. the dielectric constants of the solvents (ϵ): 1, cyclohexane; 2, dibutyl ether; 3, 1,2-dichloroethane; 4, pyridine; 5, 4-methylpentanenitrile.

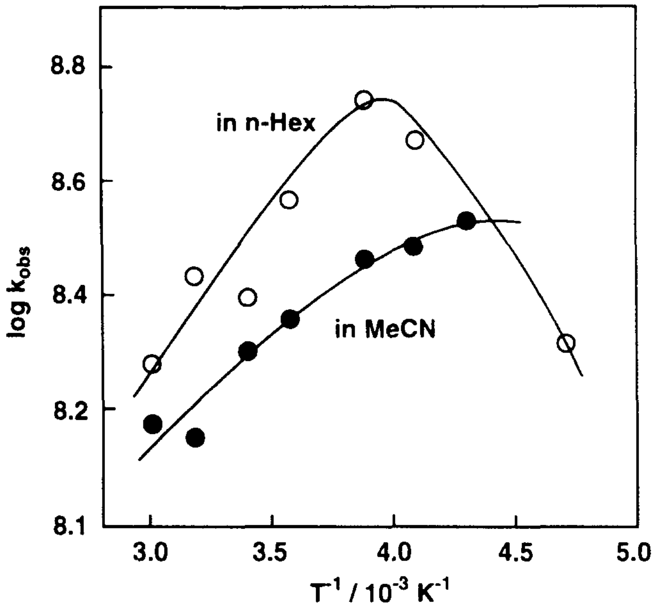

Fig. 3. Temperature dependence of the rate constant of the reaction of NY with dimethyl fumarate (k_{obs}) in n-hexane (○) and acetonitrile (●).

the concentration and k_{obs} is less than 10^3 M^{-1} s^{-1}. For vinyl acetate (IP = 9.19 eV [16]), k_{obs} is 1.3×10^4 M^{-1} s^{-1}, which deviates from the linear slope for the electron-deficient olefins as shown in Fig. 1.

2.2. Solvent effect

The 1,3-dipolar addition of NY to olefins has been reported to proceed through an NY–olefin complex [7]. Since complex formation is presumed to proceed by diffusion, the rate constant should depend on the viscosity (η) of the solvent used. Accordingly, it is expected that k_1 in MeCN ($\eta = 5.0\times10^{-4}$ P) will be considerably larger than that in c-Hex ($\eta = 9.751\times10^{-4}$ P [19]). However, the results were opposite to those expected, and k_{obs} in c-Hex was found to be 1.2–1.5 times larger than in MeCN as shown in Fig. 1. Thus k_{obs} may be dependent on the solvent polarity. Laser flash photolysis of AZ in the presence of dimethyl fumarate (DF) was carried out in various types of oxygen-saturated solvent with similar η values (c-Hex, 9.8×10^{-4} P; dibutyl ether (DBE), 6.9×10^{-4} P; 1,2-dichloroethane (DCE), 8.2×10^{-4} P; pyridine (Py), 9.5×10^{-4} P; 4-methylpentanenitrile (MVCN), 9.8×10^{-4} P (at 296 K) [19]). Since differences in the viscosities of the solvents used still remain, the k_{obs} value was normalized according to Eq. (5)

$$k' = (\eta/9.0\times10^{-4})k_{obs} \tag{5}$$

where k' is the k_{obs} value in a solvent with $\eta = 9.0\times10^{-4}$ P. When k' was plotted vs. the dielectric constant (ϵ) of the solvent, the k' value decreased on going from c-Hex to DBE and then increased with increasing ϵ value, as shown in Fig. 2.[1] The minimum k' value was expected in the solvent with $\epsilon = 3$–7.

2.3. Temperature effect

The laser flash photolysis of AZ in the presence of DF was carried out in oxygen-saturated n-hexane (n-Hex) and MeCN solutions in the temperature range 210–330 K. Arrhenius plots of k_{obs} in both solvents are shown in Fig. 3. In n-Hex, k_{obs} initially increased with increasing temperature up to 260 K and then decreased. In contrast, k_{obs} in MeCN decreased monotonically with increasing temperature. From logk_{obs} in the higher temperature range, the activation energies of the reactions were roughly calculated to be −2.2 and −1.5 kcal mol^{-1} in n-Hex and MeCN respectively. The apparent negative activation energies indicate the formation of a complex between NY and olefin which either dissociates into NY and olefin or undergoes adduct formation (Eq. (2)). Furthermore, the energy barrier must be higher for dissociation than for adduct formation.

Since the complex is presumed to be formed by diffusion ($k_1 \approx k_{diff}$) [7], Eq. (3) can be written as

$$k_{-1}/k_2(k_{diff}-k_{obs})/k_{obs} \tag{6}$$

A plot of $\log(k_{-1}/k_2)$ vs. T^{-1} provides the differential activation enthalpy ($\Delta\Delta H$) and entropy ($\Delta\Delta S$) between dissociation and product formation from the complex [7]. As shown in Fig. 4, good linear relationships were obtained for both n-Hex and MeCN. The $\Delta\Delta H$ and $\Delta\Delta S$ values at 298 K

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[1] The k' values for solvents with a low viscosity, such as n-Hex ($\eta = 3.0\times10^{-4}$ P) and MeCN ($\eta = 5.0\times10^{-4}$ P), deviate from the relationship for the series of solvents shown in Fig. 2. This suggests that the normalization in Eq. (5) may be applicable only to the viscosity range 7×10^{-4} to 1×10^{-3} P.

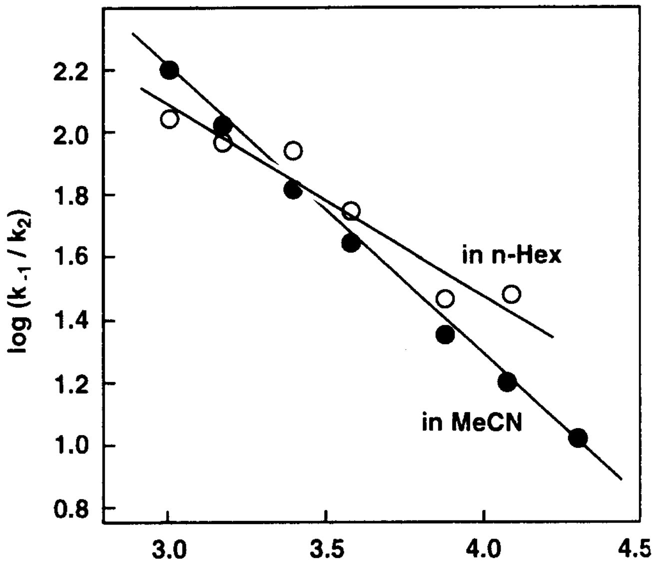

Fig. 4. Plots of log(k_{-1}/k_2) for the reaction of NY with dimethyl fumarate in *n*-hexane (○) and acetonitrile (●) vs. the reciprocal of the temperature.

were estimated from the slopes and intercepts to be -2.4 kcal mol^{-1} and -17 eu in n-Hex and -2.2 kcal mol^{-1} and -22 eu in MeCN respectively. From these values, the differences in the free energy change ($\Delta\Delta G = \Delta G_{\text{diss}} - \Delta G_{\text{prod}}$) were calculated to be 2.6 and 4.3 kcal mol^{-1} in n-Hex and MeCN respectively.

3. Discussion

The 1,3-dipolar addition of NY to various types of olefin was studied. Since NY reacts with electron-deficient olefins, providing a linear dependence of k_{obs} on IP of the olefins (see Fig. 1), it is clear that the reaction proceeds through the interaction between the NY HOMO and the dipolarophile (olefin) LUMO, similar to the reaction of phenylazide reported by Sustmann and Trill [10]. The reaction involves reversible NY–olefin complex formation, followed by adduct formation, with different energy barriers, since the temperature dependence of k_{obs} gives a negative activation energy. Solvent polarity effects on both processes produce the phenomena shown in Fig. 2.

Solvent polarity effects on the reaction rate are generally caused by the different solvation energies of the reactant, transition state and product. The solvation energy of the transition state is difficult to estimate, but the difference between the solvation energies of the reactant and product can be estimated by calculation. The degree of stabilization by solvation is related to the dipole moment of the species. Therefore when the reaction gives a product with a smaller dipole moment than the reactant, more efficient stabilization of the reactant than the product should increase the energy barrier of the reaction, leading to retardation of the reaction rate.

The dipole moments of NY and the adduct of NY with 2,3-dimethyl-2-butene (i.e. 2-(biphenyl-4-yl)-3,3,4,4-tetramethyl-1-pyrroline) were calculated to be 0.1998 D and 2.0656 D respectively. On complexation, the dipole moment of NY should be partially compensated by that of the electron-rich or electron-deficient olefin. Therefore the dipole moment of the complex is expected to be considerably smaller than that of NY, i.e. $\mu < 0.1998$ D. Furthermore, tight coordination of the olefin in the complex may prevent efficient solvation, leading to a decrease in the stabilization energy of the complex (ΔE_{comp}) relative to that for NY (ΔE_{NY}).

On the basis of the assumption described above, the stabilization energies of the three species NY, the NY–olefin complex and the product pyrroline may be written as: $\Delta E_{\text{comp}} < \Delta E_{\text{NY}} < \Delta E_{\text{prod}}$. On increasing ϵ of the solvent, both k_{-1} and k_2 should increase, while k_1 should decrease. For reactions in various solvents, the rate constants are restricted by the viscosity range.^{1} A plot of k' vs. ϵ gives a minimum in the region around $\epsilon = 3$–7 as shown in Fig. 2. The minimum may originate from the combined effects on k_1, k_{-1} and k_2. In the less polar region around $\epsilon = 2$–3, k_{obs} decreases with increasing ϵ, suggesting the dominant contribution of k_{-1}. In the highly polar region of $\epsilon > 7$, k_{obs} increases with increasing ϵ which indicates the dominant contribution of k_2. However, the reason for these results is not clear at present.

The good linear relationships in Fig. 4 allow us to compare the thermodynamic parameters $\Delta\Delta H$, $\Delta\Delta S$ and $\Delta\Delta G$ in n-Hex and MeCN. The difference between $\Delta\Delta H_{\text{MeCN}}$ (-2.2 kcal mol^{-1}) and $\Delta\Delta H_{\text{n-Hex}}$ (-2.4 kcal mol^{-1}) is not considerable. The difference between $\Delta\Delta S_{\text{MeCN}}$ (-22 eu) and $\Delta\Delta S_{\text{n-Hex}}$ (-17 eu) seems to reflect the difference between the viscosities of MeCN and n-Hex. Although a dominant contribution of k_{-1} rather than k_2 is expected in n-Hex, the polar effect on the second barrier in MeCN increases k_2. Thus the differences between k_{-1} and k_2 in the two solvents may be compensated by the similar $\Delta\Delta H$ values in n-Hex and MeCN. To clarify the reactivity of NY, the determination of the temperature dependence of k_{obs} for a series of solvent–olefin combinations is desirable. Further investigation is now in progress.

4. Experimental details

4.1. Materials

AZ was synthesized as described previously [8,9]. Fumaronitrile and DF were purified by repeated recrystallization from methanol. Dimethyl acetylene-dicarboxylate was distilled three times under an N_2 stream. AN was purified as described previously [9]. Methacrylonitrile was purified by the same method as used for AN. Methyl acrylate and methyl methacrylate were washed three times with 5% sodium hydrogen sulphite aqueous solution, three times with 3% sodium hydroxide–20% sodium chloride aqueous solution and three times with saturated sodium chloride aqueous solution. After drying over anhydrous sodium sulphate and 0.3 nm molecular sieves, the monomers were distilled twice under an N_2 stream. Styrene was washed three times with 5% sodium hydroxide aqueous solution and three times with saturated sodium chloride aqueous solution. After drying over anhydrous calcium chloride and calcium hydride, the monomer was distilled twice under an N_2 stream. Vinyl acetate was distilled twice under an N_2 stream.

Spectroscopic grades of n-Hex, c-Hex, MeCN, DCE and Py were used without further purification. DBE was dried over calcium hydride and sodium metal and distilled twice under an N_2 stream. MVCN was refluxed twice with diphosphorus pentoxide overnight. The solvent was then distilled twice under an N_2 stream.

4.2. Laser flash photolysis

The laser flash photolysis of AZ was carried out in oxygen-saturated solutions at room temperature using Lambda Physik EMG 501 and Lumonics EX-510 lasers. These excimer lasers generate 308 nm light pulses (pulse width, approximately 15 ns; energy, 100 mJ, EMG 501; 70 mJ, EX-510).

4.3. Calculation of dipole moments

The dipole moments of two structures of NY (allen-type and propagyl-type) and a model compound of the adduct (2-(biphenyl-4-yl)-3,3,4,4-tetramethyl-1-pyrroline) were calculated after geometry optimization using an *RHF/AM1* program.

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