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1,3-Dipolar Additions of a Nitrile Ylide with Carbonyl Compounds Studied by Laser Flash Photolysis of 3-(Biphenyl-4-yl)-2*H*-azirine

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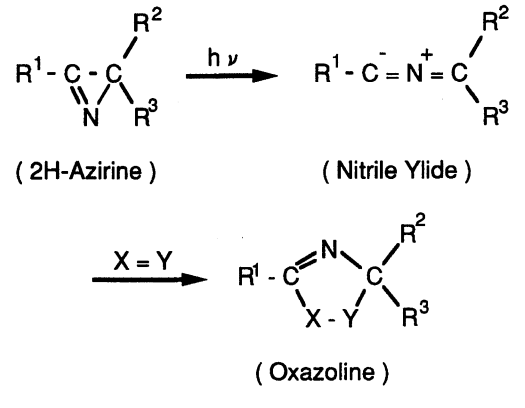
1,3-Dipolar additions of a nitrile ylide (NY) with carbonyl compounds were studied by means of the laser flash photolyses of 3-(biphenyl-4-yl)-2*H*-azirine in the presence of various types of carbonyl compounds: i.e. ketones, aldehydes, and esters. NY decays according to psuedo first-order kinetics. The rate constant of the 1,3-dipolar addition reaction of NY with carbonyl compound is increased with increasing the ionizing potential of the π-electron on the carbonyl double bond. NY reacts also with carbon dioxide ($k=5.3\times10^5$ dm^3 mol^{-1} s^{-1} in acetonitrile).

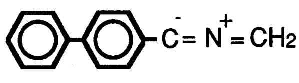
Nitrile ylide is a typical 1,3-dipole and has become a candidate for the syntheses of heterocyclic compounds.[1] This species, which is generated easily by the photoirradiation of 2*H*-azirine, has been investigated in 1,3-dipolar addition reactions with a wide variety of dipolarophiles to yield cyclic adducts (Eq. 1).[2,3] Because the 1,3-dipolar addition reactions of nitrile ylide with a carbonyl compound, such as a ketone,[4] an aldehyde,[5] an ester[6] or carbon dioxide,[7] were very important reaction to give heterocyclic compounds, those reactions have been studied with stationary irradiation of 2*H*-azirine to establish the stereo- and regioselectivities of the products.



(1)

Currently the laser flash photolysis of 2*H*-azirine is the most powerful method to study the characteristics and reactivities of nitrile ylide. Padwa and co-workers studied the 1,3-dipolar addition of nitrile ylide with olefin in detail in the laser flash photolyses of 2,2-diphenyl-2*H*-azirine and 2,3-diphenyl-2*H*-azirine.[8] They reported evidence for the presence of a new reaction intermediate nitrile ylide/olefin complex in the 1,3-dipolar addition. This species is yielded by a diffusion controlled reaction. A part of the intermediate yields the product and the other part dissociate to nitrile ylide and olefin. Recently, we measured nitrile ylide (NY, R^1=4-biphenylyl, $R^2=R^3=H$) (Chart 1) and triplet azirine directly in the 308 nm laser flash photolysis of 3-(biphenyl-4-yl)-2*H*-azirine (AZ).[9] NY has an absorption maximum at 410 nm and decays with the rate constant of 8×10 s^{-1}. For the identification of NY, the laser flash photolyses and stationary irradiation of AZ were carried out in the presence of acrylonitrile as a typical dipolarophile. The rate constant of the 1,3-dipolar addition of NY with olefin increased with increasing ionization potential of olefin.[10] Additionally, NY is a very interesting reaction intermediate for one to study the nucleophilicity of an alcohol oxygen atom and the autoprotolysis constant.[11]

In this study, the laser flash photolyses of AZ were



(Nitrile Ylide, NY)

Chart 1.

carried out in the presence of various types of carbonyl compounds in oxygen-saturated cyclohexane, to quench the triplet AZ from energy transfer. The purpose was to investigate the 1,3-dipolar addition reactions of NY dynamically. The laser flash photolysis of AZ was also carried out in the presence of carbon dioxide in acetonitrile.

Experimental

Materials. 3-(Biphenyl-4-yl)-2*H*-azirine (AZ) was synthesized and purified, as described before.[10] Propanone, 2-butanone, 2-pentanone (ketones), ethanal, propanal, butanal, 2-methylpropanal, 2,2-dimethylpropanal, ethyl acetate, methyl trifluoroacetate, and methyl chloroacetate were dried on anhydrous sodium sulfate and on 0.3 nm molecular sieves. These carbonyl compounds were purified by two distillations under a N_2 stream. Carbon dioxide was washed by passing it two times through concentrated sulfuric acid and was dried by passing it through an anhydrous calcium chloride column.

Dichloroethanal and trichloroethanal were separated from water by using anhydrous calcium chloride and ether. After being drid on anhydrous calcium chloride, these aldehydes were purified by two distillations under a N_2 stream. Spectroscopic grade cyclohexane and spectroscopic grade acetonitrile were used without further purification.

Apparatus. The laser flash photolyses were carried out at room temperature (293 K) by the aids of a Lambda Phisks EMG 501 type and a Lumonics EX-510 type. These devices generate a λ=308 nm light pulse [pulse width: ca. 15 ns, 100 mJ (EMG 501 type) or 70 mJ (EX-510 type)].

Results and Discussion

Laser flash photolyses of 3-(biphenyl-4-yl)-2*H*-azirine (AZ) were carried out in the presence of carbonyl compounds in oxygen-saturated cyclohexane. The decay traces of NY were monitored at λ=410 nm, the absorption maximum wavelength of NY. On the identification of NY, the decay rate of NY increased with increasing propanone concentration (k=2.5×10^3 dm^3 mol^{-1} s^{-1}).[9] In the laser flash photolyses of AZ in the presence of 2-butanone or 2-pentanone, the triplet AZ, which seems to be yielded by the energy transfer from the triplet carbonyl compound, was mainly measured immediately after the flash. The signal of NY was, however, too weak and unchangeable to measure the decay rate.

Next, the laser flash photolyses of AZ were carried out in the presence of various types of esters. The decay of NY could not be measured in the presence of ethyl acetate or ethyl formate, but could be in the presence of methyl chloroacetate and ethyl trifluoroacetate. The decay profiles followed pseudo-first order kinetics. The rate constants (k) were determined to be 2.1×10^5 dm^3 mol^{-1} s^{-1} (methyl chloroacetate) and 3.9×10^6 dm^3 mol^{-1} s^{-1} (ethyl trifluoroacetate) from the slope of the plot of the NY decay rate versus the dipolarophile concentration.

Third, the laser flash photolyses of AZ were carried out in the presence of aldehyde. The k values determined are listed in Table 1. The rate constants for dichloroethanal and trichloroethanal are too large: 1.6×10^8 and 4.0×10^8 dm^3 mol^{-1} s^{-1}, respectively. The k value increased as follows: 2,2-dimetylpropanal < ethanal < 2-methylpropanal < propanal < butanal < dichloroethanal < trichloroethanal.

Carbon dioxide is a typical carbonyl compound. Lastly, the laser flash photolysis of AZ was also carried out in acetonitrile after bubbling mixed gases of carbon dioxide and oxygen at 295 K. The rate constant was determined to be 5.3×10^5 dm^3 mol^{-1} s^{-1} (saturated [CO_2]=1.4×10^{-1} mol dm^{-3} in acetonitrile at 295 K[12]), as shown in Fig. 1.

Plots of logarithmic rate constant (log k) of the 1,3-

Table 1. Rection Rate Constants of NY with Carbonyl Compounds in Cyclohexane

No.	Compound	IP (n-electron)/eV[a]	IP ($\pi_{C=O}$)/eV[a]	k/dm^3 mol^{-1} s^{-1}
1	CH_3COCH_3	9.70	12.59	2.5×10^3
2	$C_2H_5COCH_3$[b]	12.26	12.66	[c]
3	n-$C_3H_7COCH_3$[b]	—	—	[c]
4	CH_3CHO	10.24	13.24	3.1×10^6
5	C_2H_5CHO	9.58	12.62[d]	6.8×10^6
6	n-C_3H_7CHO	11.35	13.4	1.3×10^7
7	i-C_3H_7CHO	—	—	3.4×10^6
8	t-C_4H_9CHO	—	—	2.4×10^6
9	$CHCl_2CHO$	10.83	14.19	1.6×10^8
10	CCl_3CHO	10.88	14.47	4.0×10^8
11	$CH_3CO_2C_2H_5$	—	—	[c]
12	$HCO_2C_2H_5$	—	—	[c]
13	$CF_3CO_2C_2H_5$	—	—	3.9×10^6
14	$CH_2ClCO_2CH_3$	10.7[e]	13.2[e]	2.1×10^5
15	CO_2	13.78	17.59	5.3×10^5

a) Ref. 18. b) Laser light was absorbed almost by the carbonyl compound. c) Decay of NY could not be measured. d) Ref. 20. e) Ref. 19.

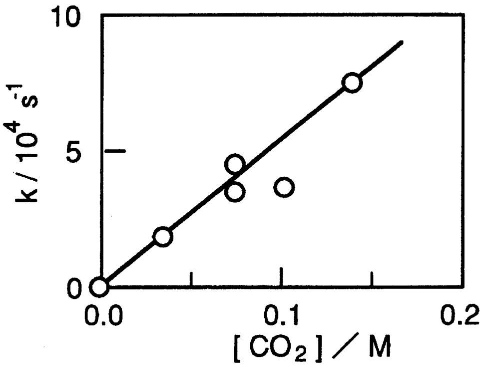


Fig. 1. Plots of the decay rate of NY vs. the CO_2 concentration.

dipolar addition against ionizating potential (IP) of the dipolarophile are known as Sustmann plots;[13,14] they indicate the electronic situation of the reaction. Because the k value on the reaction of NY with olefin increases with increasing IP of olefin, we conclude that the reaction proceeds through interaction between the HOMO level of NY and the LUMO level of olefin.[10] Although the LUMO energy of the dipolarophile is correlated linearly with its electron affinity and reduction potential, many values are reported at different conditions.[14] The LUMO energy seems to be roughly proportional to the IP value, as seen in the Sustmann plots on the reactions of phenyl azide,[15] methyl diazoacetate,[16] and benzonitrile oxide.[17] The $\log k$ value was plotted against the lowest IP value of the carbonyl compound,[18,19] as shown in Fig. 2. The plots are, unfortunately, scattered. The k of propanone and aliphatic aldehydes were, surprisingly, over three orders of magnitude larger than the rate constant estimated by means of the linear relation in the olefins, that is, the plot of the $\log k$ value vs. the lowest IP value.[10] The lowest IP of the olefin is the value of the π-electron on the double bond. On the other hand, the lowest IP value of the carbonyl compounds is the IP of the n-electron on the carbonyl oxygen atom. When the $\log k$ value was plotted against the IP value of the π-electron on the carbonyl double bond,[18,19] a good linear relationship was obtained, as shown in Fig. 2. This relation is parallel to the relation obtained in the reactions of NY with olefins, dotted line in Fig. 2.[10] Then, we concluded that the 1,3-dipolar addition of NY with carbonyl compound must proceed through the interaction between the NY-HOMO and the dipolarophile-LUMO, through the as same mechanism as in the reactions of NY with olefin.

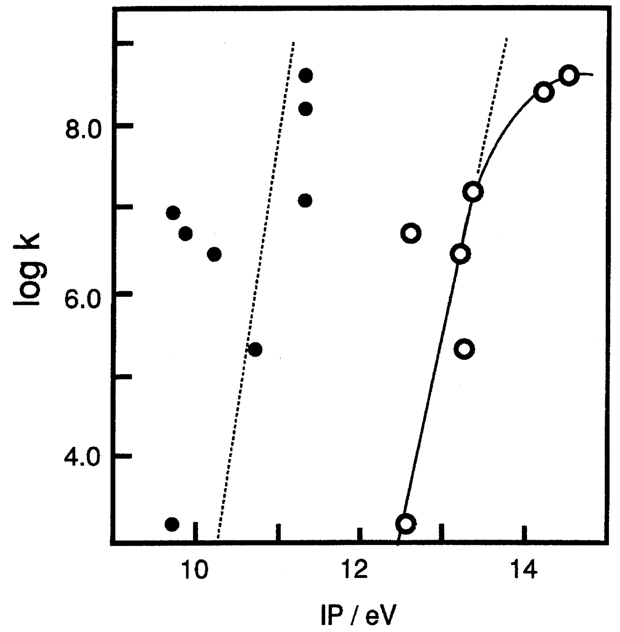
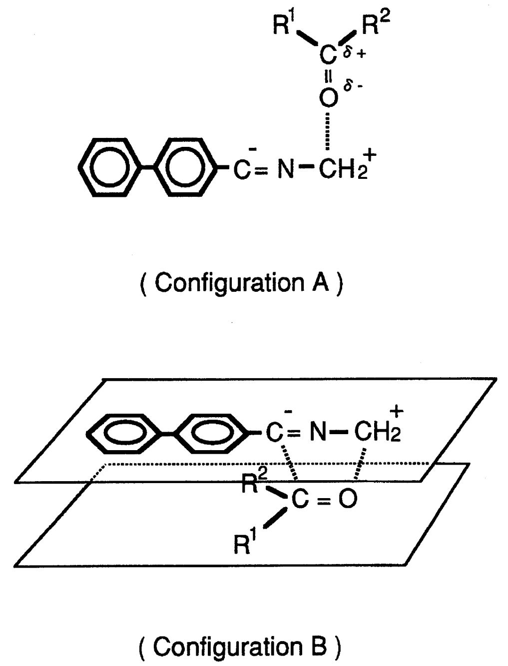


Fig. 2. Plots of the IP values of the carbonyl compound vs. $\log k$. ○: the IP value for π-electron of the carbonyl double bond, ●: the lowest IP value for carbonyl oxygen atom. The dotted line shows the relationship between the lowest IP value and $\log k$ in the reaction of NY with olefin in cyclohexane.


(Configuration A)

(Configuration B)

Scheme 1. Configurations of the complex in the 1,3-dipolar addition of NY with carbonyl compound.

There are two configurations before the addition: the carbonyl oxygen attached to a terminal carbon of NY (A) and the carbonyl double bond overlapping on the NY surface (B) (Scheme 1). The linear relation between the $\log k$ value and π-IP value indicates that the reaction proceeds through the B type configuration. Padwa et al. reported the existence of a reaction intermediate in the 1,3-dipolar addition of nitrile ylide and olefin.[8] The configuration B seems to be that of the intermediate. In the reactions with bulky carbonyl compounds, the reaction rate constants with dichloroethanal and trichloroethanal are very much smaller: 1.6×10^8 (dichloroethanal) and 4.0×10^8 $\mathrm{dm^3\,mol^{-1}\,s^{-1}}$ (trichloroethanal) than value estimated by means of the linear relation in Fig. 2 (solid line). The small rate constants may be caused by the bulkiness of aldehyde [steric parameters of alkyl group (E_s): -1.54 (dichloromethyl), -2.06 (trichloromethyl)$^{21)}$]. In the intermediate, the carbonyl surface can not easily approach the NY surface closely enough to react.

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