

INVERSE TEMPERATURE DEPENDENCE OF THE DIPOLAROPHILIC REACTIVITY OF CARBONYL YLIDE PHOTOGENERATED FROM *trans*-STILBENE OXIDE

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Summary

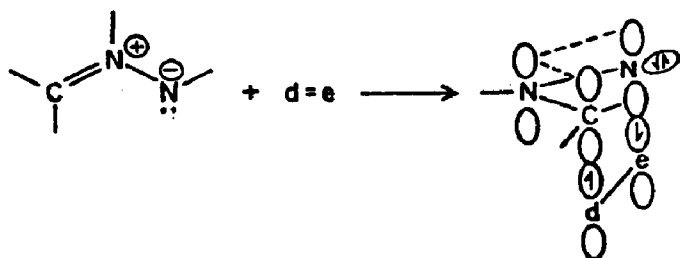
In methylcyclohexane at 295 - 353 K, cycloaddition reactions of carbonyl ylide photogenerated from *trans*-stilbene oxide have small or negative activation enthalpies. This behavior can be explained in terms of reversible formation of a bimolecular complex. The increase in reactivity from one dipolarophile to another is due to the increase in differential activation entropy for collapse and back-dissociation of the complex.

1. Introduction

The mechanism of 1,3-dipolar cycloaddition reactions has been studied [1] in great detail by both experimental and theoretical chemists. Currently the general consensus is in favor of the concerted nature [1 - 3] of these reactions, although an opposite view, *i.e.* one in favor of a two-step pathway involving a biradical intermediate, exists in the literature [3 - 5]. The concerted mechanism is supported by evidence from a large body of experimental results [1], namely the stereospecificity of cycloaddition products, negative activation entropies, small effects of solvent polarity on reaction rates, primary kinetic isotope effects (¹²C versus ¹⁴C) etc. According to Huisgen, whose contribution in the field of 1,3-dipolar cycloaddition chemistry is monumental, the formation of a "two-plane orientation complex" precedes the concerted bond-making and bond-breaking. This is illustrated here using an azomethine imine as the 1,3-dipole:

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A recent survey [1] of Eyring parameters of various 1,3-dipolar cycloadditions has shown that, while the activation entropy ΔS^\ddagger lies in the limited range from -22 to -39 entropy units, the activation enthalpy ΔH^\ddagger varies from 0 to 18 kcal mol $^{-1}$. The latter determines the temperature dependence of the rate constants. Ozone is the most reactive 1,3-dipole, characterized by temperature-independent rate constants k_r of 3.8×10^5 M $^{-1}$ s $^{-1}$ and 1.66×10^4 M $^{-1}$ s $^{-1}$ for its reaction with *trans*-stilbene and triphenylethylene respectively (in carbon tetrachloride at $15 - 35$ °C [6]). While the ΔH^\ddagger values of these reactions are approximately zero, the values for ΔS^\ddagger (-33 entropy units and -39 entropy units respectively) are in the normal range.

Recent studies [7 - 14] based on laser flash photolysis and fast kinetics measurements have shown that the reactivity of carbonyl ylides (from oxiranes) with typical dipolarophiles (*e.g.* alkene or alkyne derivatives, xanthione) can be very high. In some cases, *e.g.* with maleic anhydride and xanthione, the k_r values are in the limit of diffusion control. From a mechanistic point of view, it is of interest to know the activation parameters of these reactions. Thus, we have studied the temperature dependence of the dipolarophilic interaction of a prototype of carbonyl ylides, namely the one photogenerated from *trans*-stilbene oxide. The results are found to be rather anomalous and appear to have interesting mechanistic implications.

2. Experimental details

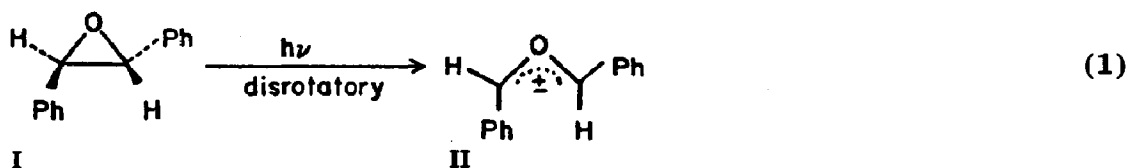
trans-Stilbene oxide, either purchased from Aldrich or prepared from *trans*-stilbene by methods given in the literature [12], was recrystallized from toluene. Dimethylacetylene dicarboxylate (DMAD) and methyl acrylate, both from Aldrich, were distilled under reduced pressure. Maleic anhydride (Fisher) was recrystallized from dichloromethane. Methylcyclohexane (Baker Chemicals) was of spectral grade and was used as received.

The laser flash photolysis experiments were carried out in a computer-controlled set-up using, for excitation, 266 nm laser pulses (about 6 ns; 10 mJ or less) from a Quanta-Ray Nd-YAG DCR-1 system. The details of the kinetics spectrophotometer and data collection system are available elsewhere [7, 13, 14]. Rectangular quartz cells of 3 mm path length were used in a front-face geometry between the directions of the laser pulses and the analyzing light. For temperature dependence studies, the cell was surrounded by a Dewar-type quartz jacket fitted with flat windows. Nitrogen gas, pre-

heated by passage through a quartz tube (filled with glass wool and heated in a tube furnace), was allowed to flow into the jacket around the photolysis cell. By regulating the flow of the hot nitrogen, the temperature (monitored by a thermocouple probe) could be controlled to within ± 1 °C.

3. Results

On 266 nm laser flash photolysis in methylcyclohexane at room temperature, *trans*-stilbene oxide (I) forms a transient species ($\lambda_{\text{max}} = 470$ nm) that decays with clean first-order kinetics ($\tau = 700$ ns). On the basis of oxygen insensitivity, comparison with absorption spectra of photogenerated ylides in glassy matrices at low temperatures [15], anticipated symmetry-controlled disrotatory ring-opening under photoexcitation [16], quenching by dipolarophiles (alkene/alkyne derivatives) and isolation of stereoselective tetrahydrofuran adducts from steady state photolysis in the presence of electron-deficient olefins [17, 18], the 470 nm transient species is assigned as the carbonyl ylide in the *exo,endo* form II [7]. A recent picosecond study [19] has shown that this species is formed in 450 ± 250 ps following the photoexcitation of *trans*-stilbene oxide by a 25 ps laser pulse (266 nm) in acetonitrile or cyclohexane:



The decay kinetics of the carbonyl ylide (470 nm species) were measured as a function of concentration of three dipolarophiles at various temperatures. Under all conditions, the transient absorption decay followed first-order kinetics. Two representative traces and their first-order fits are shown in Fig. 1. The observed rate constants k_{obs} for a given quencher at a given temperature were linearly dependent on the quencher concentration $[Q]$. Figure 2 shows several plots for methyl acrylate based on $k_{\text{obs}} = \tau_Y^{-1} + k_r[Q]$ where τ_Y is the lifetime of the ylide in the absence of a quencher and k_r is the bimolecular rate constant for its reaction with Q .

The Eyring plots for k_r with maleic anhydride, DMAD and methyl acrylate as the reactants are presented in Fig. 3, lines A - C. For DMAD and methyl acrylate, the plots show an inverse temperature dependence. The data concerning the activation enthalpy ΔH^\ddagger and the activation entropy ΔS^\ddagger are given in Table 1.

4. Discussion

Both *trans*- and *cis*-stilbene oxide have been subjected [17, 18] to steady state photolysis studies in the presence of electron-deficient alkene

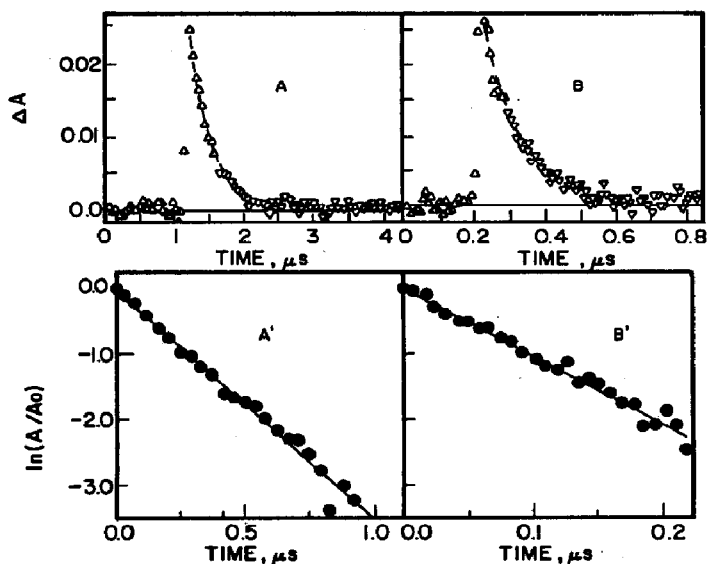


Fig. 1. Kinetics traces showing the decay of carbonyl ylide photogenerated from *trans*-stilbene oxide ($\lambda_{\text{ex}} = 266 \text{ nm}$) at 40°C in methylcyclohexane in the absence of a quencher (curve A) and in the presence of 1.11 mM maleic anhydride (curve B). The fits of the data into integrated first-order kinetics are shown in parts A' and B' respectively.

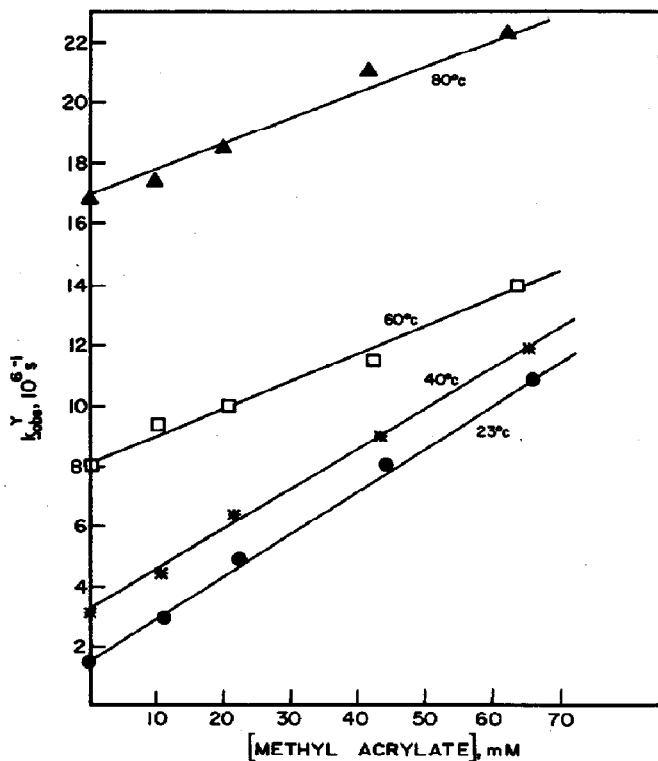


Fig. 2. The linear dependence of observed pseudo-first-order rate constants k_{obs} for ylide decay on methyl acrylate concentrations at various temperatures (solvent, methylcyclohexane).

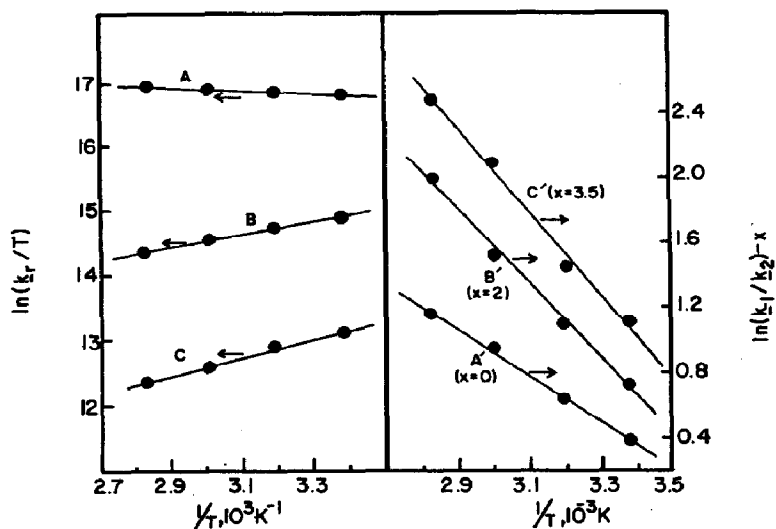


Fig. 3. Eyring plots of k_r (lines A - C) and plots of $\ln(k_{-1}/k_2)$ vs. $1/T$ (see eqn. (4b)), with maleic anhydride (lines A and A'), DMAD (lines B and B') and methyl acrylate (lines C and C') as reactants in methylcyclohexane. It should be noted that plots B' and C' are linearly displaced along the ordinate (vertical axis).

TABLE 1

Eyring parameters^a for dipolar cycloaddition of carbonyl ylide photogenerated from *trans*-stilbene oxide in methylcyclohexane

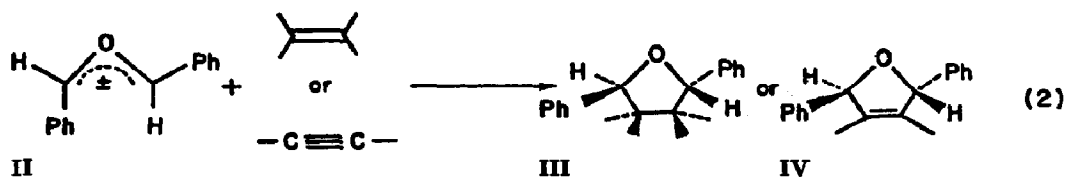
Parameter	Dipolarophile		
	Maleic anhydride	DMAD	Methyl acrylate
$10^8 k_r$ in methylcyclohexane ^b ($M^{-1} s^{-1}$)	57	8.5	1.4
$10^8 k_r$ in acetonitrile ^b ($M^{-1} s^{-1}$)	29	8.6	1.4
ΔH^\ddagger (kcal mol ⁻¹)	0.47	-2.0	-2.8
ΔS^\ddagger (entropy units)	-12	-24	-30
$\Delta\Delta H^\ddagger$ ^c (kcal mol ⁻¹)	-2.9	-4.5	-5.2
$\Delta\Delta S^\ddagger$ ^c (entropy units)	-10	-21	-27

^aMaximum variations in terms of 2σ , obtained from least-squares linear fits [20], are $\Delta H^\ddagger = \pm 0.8$, $\Delta S^\ddagger = \pm 2$, $\Delta\Delta H^\ddagger = \pm 0.8$ and $\Delta\Delta S^\ddagger = \pm 2$.

^bAt 295 K; the data in acetonitrile are taken from ref. 7.

^c $\Delta\Delta H^\ddagger = \Delta H^\ddagger_2 - \Delta H^\ddagger_{-1}$ and $\Delta\Delta S^\ddagger = \Delta S^\ddagger_2 - \Delta S^\ddagger_{-1}$ (see eqns. (3) and (4)).

derivatives as dipolarophilic traps (for carbonyl ylides). Under direct excitation [17, 18] as well as under triplet [17] and electron transfer [18] sensitization, tetrahydrofurans have been isolated as 1,3-dipolar cycloaddition products. There is little room for doubt about the fact that 1,3-dipolar addition



is responsible for the observed quenching of the carbonyl ylide (470 nm) under examination.

The negative temperature dependence of a bimolecular reaction rate is usually indicative of a composite mechanism [21]. Specifically, involving organic photointermediates, there are several examples in the literature where zero or negative activation enthalpies have been observed and explained in terms of reversible formation of a bimolecular complex. These include cycloaddition of singlet carbenes with alkenes [22], 4-carboxymethylbenzophenone phosphorescence quenching by 2,3-dimethyl-2-butene [23], reaction of singlet oxygen with enol esters [24], and polyenal triplet quenching di-*tert*-butylnitroso radical [25]. Recently, while the present work was in progress, a report [26] appeared describing the inverse temperature dependence of the reaction of a nitrile ylide ($C_6H_5C\equiv\dot{N}-\bar{C}HC_6H_5$) with olefins. Similar behavior has been observed [27] for the alkene quenching of a transient species photogenerated from 9-diazofluorene in acetonitrile. This transient ($\lambda_{max} = 470$ nm) was originally thought to be triplet fluorenylidene [27] but the assignment has now been revised [28] in favor of a nitrile ylide derived from the carbene and acetonitrile.

The present kinetics data can be analyzed in terms of the reversible formation of a complex between the carbonyl ylide (Y) and a dipolarophile (D):



$$k_r = k_1 \frac{k_2}{k_{-1} + k_2} \quad (5)$$

Identifying k_1 as the rate constant for diffusion (given by $k_{diff} = 8RT/2000\eta$), k_{-1}/k_2 can be calculated on the basis of a rearranged form of eqn. (5). Figure 3, lines A' - C', shows the temperature dependence of k_{-1}/k_2 . The differential activation parameters obtained from the plots in Fig. 3, lines A' - C', are given in Table 1. Evidently, on going from the slow quencher (methyl acrylate) to the fast one (maleic anhydride), both $\Delta\Delta H^\ddagger$ and $\Delta\Delta S^\ddagger$ become less negative. Thus, among the three dipolarophiles, the higher value for k_r at a given temperature is due to the increase in $\Delta\Delta S^\ddagger$ (leading to smaller k_{-1}/k_2) which more than compensates for a corresponding increase in $\Delta\Delta H^\ddagger$. Interestingly, this behavior differs from that in the case of dipolarophilic reactivity [26] of the nitrile ylide, $C_6H_5C\equiv\dot{N}-\bar{C}HC_6H_5$, where $\Delta\Delta H^\ddagger$ and $\Delta\Delta S^\ddagger$ are

found to increase and decrease respectively, on going from a fast to a slow quencher.

In conclusion, the inverse temperature dependence behavior of the 1,3-dipolar addition of the carbonyl ylide suggests the involvement of a short-lived complex intermediate. However, there is no basis for us to assign the latter to the "two-plane orientation complex" (proposed by Huisgen [1 - 3]) or the 1,5-biradical (proposed by Firestone [4, 5]). An intermediate zwitterionic in nature or characterized by a great deal of charge separation is ruled out by the fact that on going from a non-polar solvent (methylcyclohexane) to a polar solvent (acetonitrile), k_r either decreases or remains almost unchanged (Table 1).

Acknowledgments

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