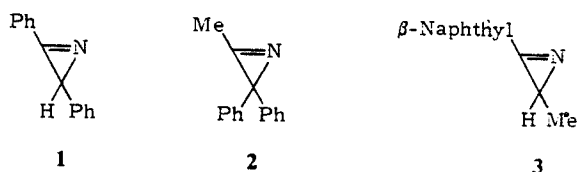


Kinetics of the Reaction of Electron Deficient Olefins with Nitrile Ylides Generated by Laser Flash Photolysis of Substituted Azirines**

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Dedicated to Professor G. O. Schenck on the occasion of his 70th birthday

In view of the traditional importance of nitrile ylides as intermediates in azirine photochemistry^[1] and the new attention that these species have acquired as possible intermediates in carbene chemistry^[2], we have initiated a pulsed laser transient absorption study of a series of azirines 1–3. The nitrile ylides derived from these azirines have been characterized both in terms of their optical absorption spectra and absolute rates of reactivity, and as possible intermediates in carbene chemistry.



Pulsed laser photolysis of Ar-purged isooctane solutions of 1–3 at 25°C resulted in the production of intense, long-lived ($\tau > 100 \mu\text{s}$) absorptions over the range 250–400 nm. Absorption spectra taken ca. 5 μs after the laser pulse are in excellent agreement with those obtained at 77 K (Table 1). While laser photolysis of azirines 1 and 3 gave rise to absorptions attributable to nitrile ylides only, azirine 2 yielded a signal of an additional short-lived intermediate in the range 300–320 nm. This species, unlike the ylides, was quenched by O_2 ($k_q = 2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$), thus allowing us to obtain the spectrum of the ylide alone. Subtraction of the O_2 -purged spectrum from the Ar-purged spectrum (after normalization at 370 nm) resulted in a spectrum of the short-lived intermediate with $\lambda_{\text{max}} = \text{ca. } 305 \text{ nm}$; this corresponds well with that of diphenyl carbene produced by other routes^[3]. It is important that the ylide absorption obtained from azirine 2 is not observed upon pulsed laser photolysis of diphenyl carbene precursors in acetonitrile solvent. This is in contrast to the observation of an ylide, formed by addition of the free carbene to the nitrile solvent, upon laser flash photolysis of 9-diazofluorene in acetonitrile^[2]. Evidently, the rate constant for reaction of acetonitrile with diphenyl carbene is significantly smaller than that of acetonitrile with fluorenylidene.

Table 1. Absorption maxima and rate constants of the subsequent reactions of the primary photolysis products of azirines 1–3.

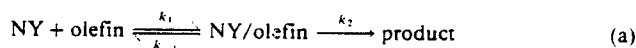
Azirine	λ_{max} (77 K) [nm] [a]	λ_{max} (298 K) [nm] [b]	k_q [d] (acrylonitrile) [$\text{M}^{-1} \text{ s}^{-1}$]	k_q [d] (fumaronitrile) [$\text{M}^{-1} \text{ s}^{-1}$]	k_{rel} (acrylonitrile, fumaronitrile)
1	346	345	$(1.22 \pm 0.03) \times 10^6$	$(1.09 \pm 0.07) \times 10^9$	890 ± 100
2	368	305 [c], 360	$(1.0 \pm 0.3) \times 10^6$	$(5.4 \pm 0.3) \times 10^8$	540 ± 200
3	277	280	$(5.4 \pm 0.3) \times 10^6$	$(7.4 \pm 0.8) \times 10^9$	1370 ± 200

[a] Steady-state photolysis (1000 W Xe/Hg arc lamp equipped with a high intensity monochromator: $\lambda_{\text{exc}} = 248 \pm 10 \text{ nm}$) of ca. 10^{-5} M azirine in Ar-purged 3-methylpentane. [b] Laser flash photolysis (Lambda Physik EMG 101 Excimer Laser, 248 nm, 15 ns pulse width) of ca. 10^{-5} M azirine in Ar-purged isooctane. [c] This absorption is quenched by O_2 (see text). [d] Conditions are the same as in [b], except that azirine, 1, was excited at 308 nm (20 ns pulse width).

In the absence of quenchers the observed transient decays for each ylide exhibit both first and second order components; however, pulsed laser photolysis of azirines 1–3 in the presence of electron deficient olefins in O_2 -saturated isooctane solution resulted in quenching of the transient absorption. At sufficiently high olefin concentrations, the decay of the transient obeyed clean first-order kinetics. Under these experimental conditions, plots of the observed first-order rate for ylide decay as a function of olefin concentration were linear, and their slopes gave the bimolecular quenching rate constant, k_q . The rate constants for quenching by acrylonitrile and fumaronitrile are listed in Table 1. For azirine 1 the relative quenching rates of fumaronitrile and acrylonitrile have been reported in the literature from steady-state trapping experiments^[4]. This value (1070 ± 100) is the same, within experimental error, as that obtained from our absolute rate constants (890 ± 100).

The rate constants k_q for the reaction of the nitrile ylide derived from 1 with methyl acrylate and diethyl fumarate were studied as a function of temperature. The resulting Arrhenius plots after correction for solvent contraction indicate that k_q for methyl acrylate is essentially insensitive to temperature ($E_a \approx 0 \text{ kcal/mol}$), while the quenching rate

constant for diethyl fumarate initially increases with decreasing temperature ($E_a \approx -1.5 \text{ kcal/mol}$) and begins to decrease at temperatures below ca. -65°C . This type of Arrhenius behavior has been observed previously for the quenching of phosphorescence from ketones, carbenes, and singlet oxygen^[5]. A kinetic scheme which fits this behavior is given in eq. (a), where NY is the nitrile ylide and NY/olefin is a nitrile ylide/olefin complex:



Assuming steady-state kinetic behavior for the complex, the observed first-order quenching rate constant, k_q , can be expressed in terms of the above rate constants to give eq. (b):

$$k_q = \frac{k_1 k_2}{k_{-1} + k_2} \quad (\text{b})$$

Rearrangement of this equation gives the ratio of the rates for dissociation and collapse to product for the ylide/olefin complex [eq. (c)]. Assuming that complex formation is diffusion controlled (i.e., $k_1 = k_{\text{diff}}$), calculation of the diffusion rate constant at the temperatures at which k_q was obtained yields values for the ratio k_{-1}/k_2 from eq. (c):

$$k_{-1}/k_2 = \frac{k_1 - k_q}{k_q} \quad (\text{c})$$

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A plot of $\lg k_{-1}/k_2$ versus $1/T$ was found to yield a straight line (Fig. 1), whose slope yields the difference in the activation parameters for product formation and dissociation of the complex (i.e., $\Delta\Delta G^\ddagger = \Delta G_{\text{prod}}^\ddagger - \Delta G_{\text{diss}}^\ddagger$). As expected, the free energy requirement for reaction versus dissociation is greater for the slower quencher methyl acrylate

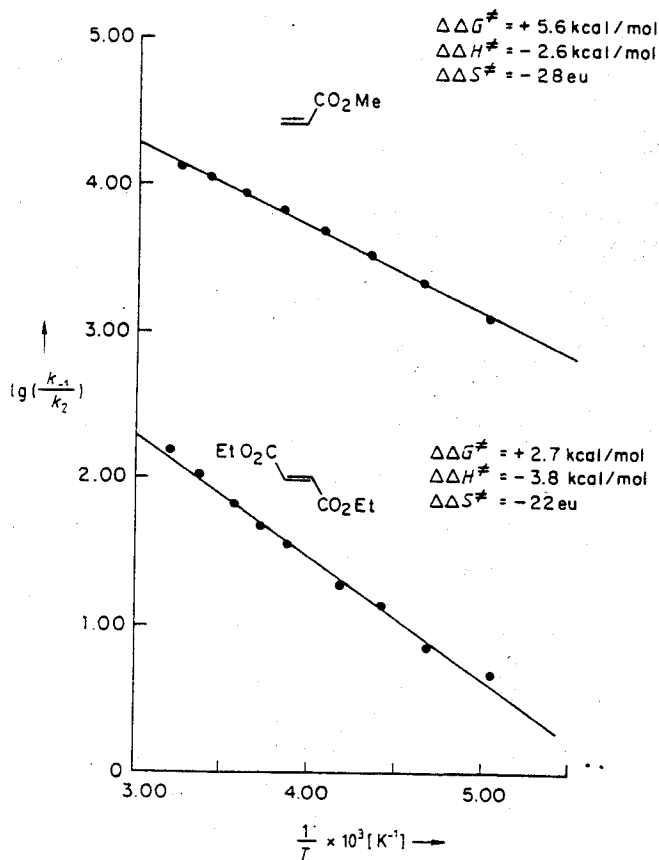


Fig. 1. Plot of $\lg(k_{-1}/k_2)$ against $1/T$ ($\Delta\Delta G^\ddagger$ calculated at $T=298 \text{ K}$).

than for the faster quencher, diethyl fumarate; however, it is noteworthy that the bulk of this free energy difference, $\Delta\Delta G^\ddagger$, results from differences in the activation entropy rather than enthalpy.

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1, 16483-98-0; 2, 65817-54-1; 3, 51051-84-4; acrylonitrile, 107-13-1; fumaronitrile, 764-42-1; methyl acrylate, 96-33-3; diethyl fumarate, 623-91-6.

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