Brief Communications

Ene reaction between 4-phenyl-1,2,4-triazoline-3,5-dione and hex-1-ene. The enthalpies, entropies, and volumes of activation and reaction in solution

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The rates of an ene reaction between 4-phenyl-1,2,4-triazoline-3,5-dione and hex-1-ene were studied in a temperature range of 15—40 °C and in a pressure range of 1—2013 bar. The enthalpy of reaction in 1,2-dichloroethane (-158.2 ± 1.0 kJ mol^{-1}), the enthalpy (51.3 ± 0.5 kJ mol^{-1}), entropy (122 ± 2 J mol^{-1} K^{-1}), and volume of activation (-31.0 ± 1.0 cm^3 mol^{-1}), and the volume of this reaction (-26.6 ± 0.3 cm^3 mol^{-1}) were determined. The high exothermic effect of the reaction suggests its irreversibility.

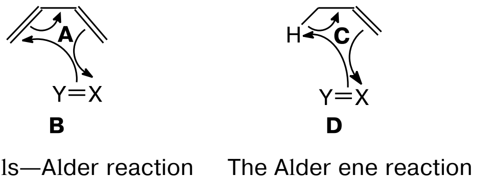
Key words: ene reaction, 4-phenyl-1,2,4-triazoline-3,5-dione, hex-1-ene, kinetics, thermochemistry, high pressure.

The Alder ene reactions occur between an alkene reactant having an allylic H atom and enophiles containing C=C, C=O, or C=N bonds activated by electron-withdrawing substituents[1] (Scheme 1).

The use of various catalysts[2—5] provides great scope for the synthesis of many potentially useful (including optically active) products. In the absence of catalysts, heating (~100 °C) is required to initiate these reactions, which makes most kinetic data uncertain.

The double N=N bond in 4-phenyl-1,2,4-triazoline-3,5-dione (**1**) is reactive in [4+2], [3+2], and [2+2] cycloadditions as well as in the Alder ene reaction.[6,7] The much better reactivity of compound **1**, which is ~10^5 times higher than that of its structural analog *N*-phenylmaleimide with the C=C bond, has been attributed[8] to the lower dissociation energy of the N=N bond (418 kJ mol^{-1}) com-

Scheme 1



A is diene, **B** is dienophile, **C** is ene, and **D** is enophile.

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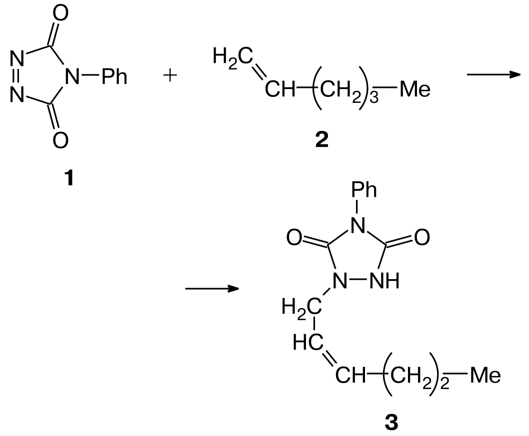
pared to that of the C=C bond (611 kJ mol^{-1}). Alkenes containing an allylic proton with the possibility of shifting their C=C bond readily and quantitatively react with diazene **1** in the ene synthesis. In this context, such reactions can be classified as "click chemistry" processes. A reaction of diazene **1** with hex-1-ene (**2**) only yields product **3** with a proven[6] structure (Scheme 2).

Scheme 2



The mechanism of these reactions can further be elucidated by analyzing the ratio of the volume of activation to the volume of reaction ($\Delta V^{\neq}/\Delta V_{r-n}$). High hydrostatic pressure has been shown[9—13] to influence the rate of high-temperature ene reactions involving the C=C and C=O bonds in an enophile, so experimental $\Delta V^{\neq}$ values measured at high temperatures should be converted to standard conditions (25 °C, 1 bar). The $\Delta V^{\neq}/\Delta V_{r-n}$ ratio can be used to compare its values for the ene and Diels—Alder reactions (for the latter, the cyclic mechanism of the transition state has been reliably proved). The $\Delta V^{\neq}$ and ΔV_{r-n} values themselves allow estimation of an increase in the rate and equilibrium constants under the high-pressure conditions of ene reactions.

The high rate of the reaction enables one to obtain reliable values of the enthalpy of reaction in solution and compare them with known values[8] for the Diels—Alder reaction.

Data on the effects of temperature and pressure on the rate of the reaction (see Scheme 2) are lacking in the literature. The rate constants k_2 obtained for the reaction in toluene under normal pressure are tabulated below.

T/°C	k_2 /L mol^{-1} s^{-1}
15	0.00114
25	0.00237
	0.00233
	0.00235
	0.00232
40	0.00690

Table 1. The rate constants k_2 of the reaction (see Scheme 2) in toluene under elevated hydrostatic pressures P

P/bar	k_2/L mol^{-1} s^{-1}	$\ln(k_p/k_{p=1})$
1	0.00204	0
214	0.00285	0.336
431	0.00369	0.592
628	0.00447	0.784
816	0.00544	0.980
1025	0.00671	1.190
1313	0.00840	1.415
1618	0.01050	1.638
2013	0.01360	1.898

The activation parameters (enthalpy, entropy, and Gibbs energy) of the reaction (see Scheme 2) have the following values: $\Delta H^{\neq} = 51.8\pm1.0$ kJ mol^{-1}, $\Delta S^{\neq} = -122\pm3$ J mol^{-1} K^{-1}, and $\Delta G^{\neq} = 88.1\pm1.0$ kJ mol^{-1}.

The rate constants at elevated pressures are given in Table 1.

The volume of activation $\Delta V^{\neq}_{\text{corr}}$ corrected for the compressibility of the solvent is -31.0 ± 1.1 cm^3 mol^{-1}. The volume of reaction ($\Delta V_{r-n} = -26.6\pm0.3$ cm^3 mol^{-1}) is appreciably smaller than the volume of activation. It should be noted that close values of these parameters have been obtained[14] for a reaction of diazene **1** with cyclohexene ($\Delta V^{\neq}_{\text{corr}} = -29.1\pm0.5$ cm^3 mol^{-1}, $\Delta V_{r-n} = -25.0\pm0.4$ cm^3 mol^{-1}). The reactions of compound **1** with hex-1-ene and cyclohexene show the same ratio of the volume parameters ($\Delta V^{\neq}_{\text{corr}}/\Delta V^{\neq}_{r-n} = 1.16$). Since the solvent only slightly affects the rate of ene reactions, which are rapid in nonpolar media,[15] one can rule out the electrostriction of the solvent in the solvation of the activated complex. The data obtained ($\Delta V^{\neq}_{\text{corr}}/\Delta V_{r-n} > 1$) suggest that the activated complex has a smaller volume than the reaction product, probably because the cyclic transition state is more ordered than the linear structure of adduct **3**. This conclusion agrees with the previous data for ene reactions involving the C=O bond of an enophile:[12,13] $\Delta V^{\neq}_{\text{corr}}/\Delta V_{r-n}$ (converted to 25 °C) = 1.1—1.3, which is also greater than unity.

The reaction studied is highly exothermic (-158.2 ± 1.0 kJ mol^{-1}) and hence can be believed to occur irreversibly under normal conditions.

Experimental

Hex-1-ene (99+%, Acros) was used as purchased. 4-Phenyl-1,2,4-triazoline-3,5-dione (97%, Aldrich, Germany) was sublimed at 100 °C and 100 Pa. The structure of product **3** had been proved earlier.[6]

The rate of the reaction in toluene was determined from the changes in the absorption band of reactant **1** with $\lambda_{\max} = 540$ nm ($\varepsilon_{540} = 245$ L mol^{-1} cm^{-1}); compounds **2** and **3** are optically transparent at this wavelength. The data obtained in a temperature range of 15—40 °C are given above. The rates of the reaction under elevated pressure were measured as described earlier.[8] The volume of reaction at 25 °C ($\Delta V_{\text{r-n}} = -26.6\pm0.3$ cm^3 mol^{-1}) was calculated from the relationship between the specific volume of the working solution of reactants **1** and **2** and the concentration of adduct **3** during the reaction (Eq. (1)). The plot of $1/d_t$ *vs.* $C_{3,t}$ keeps linear up to the 100% conversion (Fig. 1).

$$1/d_t = 1/d_{t=0} + C_{3,t}\Delta V_{\text{r-n}}/(1000d_{t=0}). \qquad (1)$$

For all measurements of the reaction rates under elevated pressure, working solutions of reactants **1** (20.2 mmol L^{-1}) and **2** (262 mmol L^{-1}) were prepared and mixed in equal volumes (1 mL each). The kinetic curves of the reaction for different elevated pressures are shown in Fig. 2. The effect of the pressure on the rate constant is illustrated in Table 1. The experimental plot of $\ln(k_p/k_{p=1})$ *vs.* P (Fig. 3) obeys equation (2).

$$\ln(k_p/k_{p=1}) = 0.00133938P - 0.00000021P^2 \qquad (2)$$

$(R^2 = 0.9989)$.

The apparent volume of activation ($\Delta V^{\neq}_{\text{app}} = -33.2\pm1.1$ cm^3 mol^{-1}) at $P = 1$ bar was calculated by formula (3).

$$\Delta V^{\neq}_{\text{app}} = -RT\partial\ln(k_P)/\partial P. \qquad (3)$$

The corrected volume of activation ($\Delta V^{\neq}_{\text{corr}} = -31.0\pm1.1$ cm^3 mol^{-1}) was calculated with allowance for the compressibility of toluene under pressure (4).

$$\Delta V^{\neq}_{\text{corr}} = -RT\partial\ln(k_P)/\partial P + (n-1)RT\beta_T, \qquad (4)$$

where k_P is the reaction rate constant at pressure P while considering the solvent incompressible, $(n-1)RT\beta_T$ is the correction for the compressibility of the solvent, n is the order of the reaction, and $\beta_T = \partial\ln(d)/\partial P$ is the compressibility of the solvent ($90\cdot10^{-6}$ bar^{-1} for toluene at 25 °C).[16]

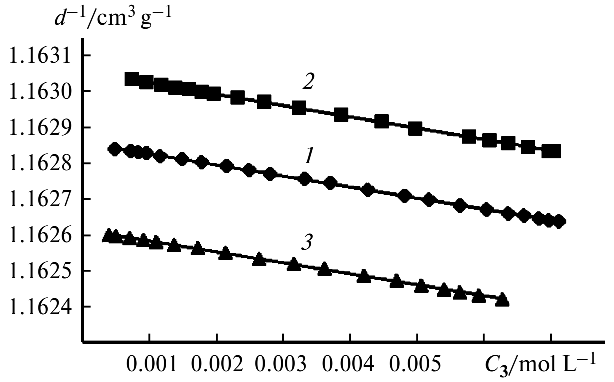


Fig. 1. Plots of d^{-1} *vs.* C_3 (see Eq. (1)) for the reaction (see Scheme 2) in toluene at 25±0.002 °C: (*1*) $d^{-1} = -0.030935C_3 + 1.162857$, $R^2 = 0.9997$, $C_{01} = 6.986\cdot10^{-3}$ mol L^{-1}, $C_{02} = 0.12495$ mol L^{-1}, $\Delta V_{\text{r-n}} = -26.6$ cm^3 mol^{-1} (for clarity, straight line *1* is shifted down the Y axis by 0.0002); (*2*) $d^{-1} = -0.031638C_3 + 1.163056$, $R^2 = 0.9997$, $C_{01} = 7.172\cdot10^{-3}$ mol L^{-1}, $C_{02} = 0.1246$ mol L^{-1}, $\Delta V_{\text{r-n}} = -27.2$ cm^3 mol^{-1}; (*3*) $d^{-1} = -0.030409C_3 + 1.162612$, $R^2 = 0.9994$, $C_{01} = 6.90\cdot10^{-3}$ mol L^{-1}, $C_{02} = 0.1114$ mol L^{-1}, $\Delta V_{\text{r-n}} = -26.2$ cm^3 mol^{-1}.

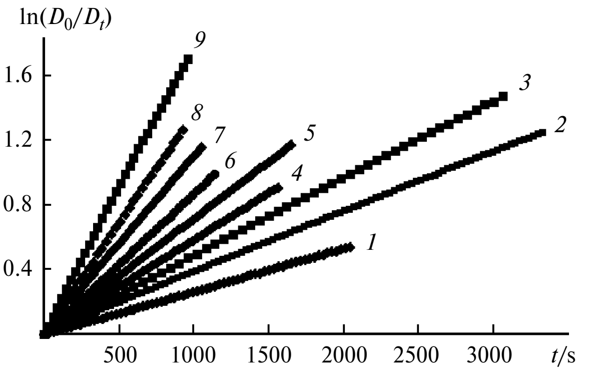


Fig. 2. Kinetic curves for the reaction (see Scheme 2) at 25 °C and P = 1 (*1*), 214 (*2*), 431 (*3*), 628 (*4*), 816 (*5*), 1025 (*6*), 1313 (*7*), 1618 (*8*), and 2013 bar (*9*).

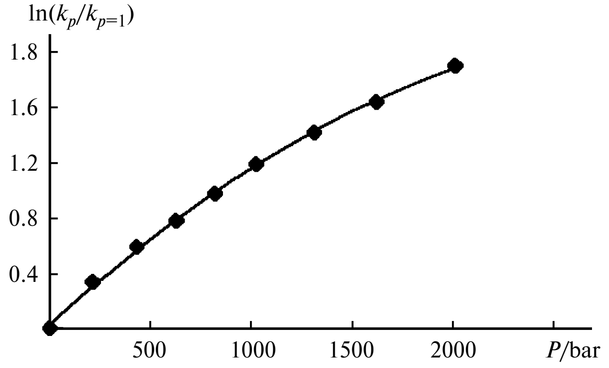


Fig. 3. Plot of $\ln(k_p/k_{p=1})$ *vs.* P for the reaction (see Scheme 2) in toluene at 25 °C.

The enthalpy of the reaction (see Scheme 2) in 1,2-dichloroethane at 25 °C was measured by calorimetry as described earlier.[8] Crystals of compound **1** (25—35 mg) were added to a solution of hex-1-ene in 1,2-dichloroethane (150 mL, C_2 = 1.0 mol L^{-1}). Three successive measurements of the heat effect gave −136.1, −135.1, and −137.8 kJ mol^{-1}. The enthalpy of dissolution of a solid sample of **1** in 1,2-dichloroethane makes a contribution of 21.9 kJ mol^{-1}, so the average enthalpy of the reaction (see Scheme 2) in solution is −158.2±1.0 kJ mol^{-1}. This exothermic effect is appreciably greater than those obtained for the Diels—Alder reactions of compound **1** with anthracene (−97 kJ mol^{-1}) and cyclopentadiene (−134 kJ mol^{-1}), yet being lower than the enthalpy of a reaction of compound **1** with buta-1,3-diene (−201 kJ mol^{-1}).[8]

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