

SHORT
COMMUNICATIONS

Enthalpy and Entropy of Activation and the Heat Effect of the Ene Reaction between 4-Phenyl-1,2,4-triazoline-3,5-dione and 2,3-Dimethyl-2-butene in Solution

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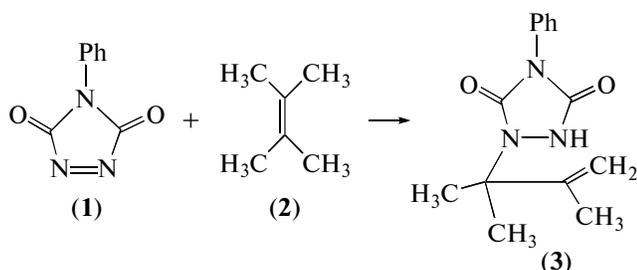
Abstract—The rate of the fastest ene reaction between 4-phenyl-1,2,4-triazoline-3,5-dione (**1**) and 2,3-dimethyl-2-butene (**2**) is studied by means of stopped flow in solutions of benzene ($k_2 = 55.6 \pm 0.5$ and $90.5 \pm 1.3 \text{ L mol}^{-1} \text{ s}^{-1}$ at 23.3 and 40°C) and 1,2-dichloroethane ($335 \pm 9 \text{ L mol}^{-1} \text{ s}^{-1}$ at 23.5°C). The enthalpy of reaction ($-139.2 \pm 0.6 \text{ kJ/mol}$ in toluene and $-150.2 \pm 1.4 \text{ kJ/mol}$ in 1,2-dichloroethane) and the enthalpy ($20.0 \pm 0.5 \text{ kJ/mol}$) and entropy ($144 \pm 2 \text{ J mol}^{-1} \text{ K}^{-1}$) of activation are determined. A clear correlation is observed between the reaction rate and ionization potential in a series of ene reactions of 4-phenyl-1,2,4-triazoline-3,5-dione with acyclic alkenes.

Keywords: ene synthesis, 4-phenyl-1,2,4-triazoline-3,5-dione, 2,3-dimethyl-2-butene, thermochemistry, kinetics.

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INTRODUCTION

4-Phenyl-1,2,4-triazoline-3,5-dione (**1**) actively participates in (4 + 2)-, (2 + 2)- reactions of cycloaddition and ene reactions of addition along N=N bonds [1]. The enhanced activity of **1** in the Diels–Alder reaction relative to the C=C analog *N*-phenylmaleimide is explained by the easier rupturing of N=N bonds (418 kJ/mol) relative to C=C bond (611 kJ/mol) [2]. Alkenes, which have an allylic proton and the ability to shift C=C bonds, readily participate in ene reactions. There are data on the rate of the reaction between active enophile **1** and a wide range of alkenes. In the reaction between **1** and 2,3-dimethyl-2-butene (**2**), only product (**3**) is formed. Its structure was determined in [1]:



The reaction product is formed in considerable amounts during the mixing of even dilute solutions of

the reactants. In this work, the rate of reaction **1** + **2** → **3** was measured using the stopped-flow approach, and the parameters of activation and the heat effect of the reaction were determined. Possible reasons for the high rate of reaction between **1** and tetramethylethylene were discussed.

EXPERIMENTAL

4-Phenyl-1,2,4-triazoline-3,5-dione (Aldrich, Germany; 97%) was sublimed prior to measurements at 100°C and 100 Pa. The purity of triazolinedione **1** was verified using the familiar absorption coefficient ($\epsilon_{532} = 171$ in 1,4-dioxane at 25°C [3]), and by its titration with 9,10-dimethylantracene, which reacts with **1** rapidly, quantitatively and irreversibly [2]. 2,3-Dimethyl-2-butene (Sigma-Aldrich, >98%) was used for our measurements without further purification. Solvents were purified using the procedures described in [4].

Conventional methods for monitoring the rate of reaction **1** + **2** → **3** proved to be unsuitable, due to its completion while mixing the reagent solutions. The reaction rate was then measured using the stopped-flow approach on a Cary 50 Bio spectrophotometer equipped with an RX 2000 unit (step, 12.5 ms) in benzene at 23.3 and 40.1°C, and in 1,2-dichloroethane at 23.5°C. The progress of the reaction was monitored

Table 1. Values of the rate constants for reaction $1 + 2 \rightarrow 3$, (k_2 , $l \text{ mol}^{-1} \text{ s}^{-1}$), correlation coefficient of kinetic dependence (R), number of experimental points (N)

Number of double	Benzene, 23.3°C			Benzene, 40.1°C			1,2-Dichloroethane, 23.5°C		
	k_2	R	N	k_2	R	N	k_2	R	N
1	55.8	0.9998	64	88.1	0.9999	50	316	0.9999	17
2	56.7	0.9999	64	91.2	0.9999	45	330	0.9998	16
3	56.3	0.9998	64	91.7	0.9999	43	341	0.9999	15
4	56.3	0.9998	63	91.8	0.9999	43	342	0.9998	15
5	54.3	0.9999	63	85.8	0.9999	50	339	0.9999	16
6	55.7	0.9997	65	92.1	0.9999	42	340	0.9998	16
7	55.8	0.9998	64	90.4	0.9999	44	340	0.9999	15
8	55.4	0.9999	65	90.5	0.9999	44	343	0.9999	15
9	55.2	0.9998	65	91.7	0.9999	44	349	0.9999	15
10	55.0	0.9999	66	91.9	0.9999	44	312	0.9999	18
$k_{2, \text{av}}$	55.6 ± 0.5			90.5 ± 1.3			335 ± 9		

using the change in the absorbance of **1** at a wavelength of 540 nm, where alkene **2** and reaction product **3** are optically transparent. The linear dependence $\ln D_{1-t}$ was observed up to reaction completeness of 75% or above. Our stock concentration of triazolinedione **1** was $8.13 \times 10^{-3} \text{ mol L}^{-1}$, while that of tetramethylethylene **2** was $8.86 \times 10^{-2} \text{ mol L}^{-1}$. All kinetic measurements were performed repeatedly to verify the reliability of the kinetic data. Filling the syringes with solutions of reagents **1** and **2** allowed us to conduct ten repeated measurements. The accuracy of measuring the rate constants was $\pm 3\%$; that of measuring the activation enthalpy was $\pm 2 \text{ kJ mol}^{-1}$; and that of measuring the entropy of activation was $\pm 6 \text{ J mol}^{-1} \text{ K}^{-1}$. The obtained data are collected in Table 1.

The enthalpy of reaction was measured by introducing samples (25–35 mg) of crystals of triazolinedione **1** into a solution of tetramethylethylene **2** (150 mL, $c_{02} = 0.022 \text{ mol L}^{-1}$) in the calorimeter cell. The operating procedure was described in [2]. The following values were obtained for three consecutive measurements: -121.9 , -120.3 , $-120.6 \text{ kJ mol}^{-1}$ in toluene, and -127.1 , -130.2 , $-127.4 \text{ kJ mol}^{-1}$ in 1,2-dichloroethane. Allowing for the heat of dissolution of crystals of **1** in toluene (18.3 kJ mol^{-1}) and 1,2-dichloroethane (21.9 kJ mol^{-1}), the values of the enthalpy of reaction $1 + 2 \rightarrow 3$ are $-139.2 \pm 0.6 \text{ kJ mol}^{-1}$ in toluene and $-150.2 \pm 1.4 \text{ kJ mol}^{-1}$ in 1,2-dichloroethane. The operation of the calorimeter was verified by measuring the heat of dissolution of potassium chloride in water

at 25°C. The obtained values ($17.4 \pm 0.2 \text{ kJ mol}^{-1}$) are consistent with data from precision calorimetry ($17.514 \pm 0.008 \text{ kJ mol}^{-1}$) [5].

RESULTS AND DISCUSSION

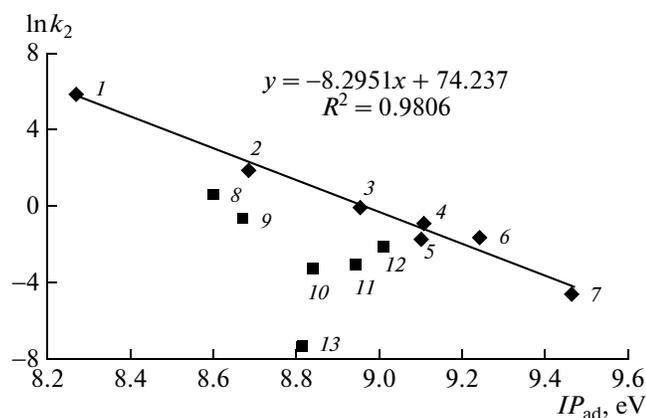
A great deal of data on the rate of ene reactions between triazolinedione **1** and different alkenes have been amassed [1, 6]. The investigated reaction $1 + 2 \rightarrow 3$ was the fastest one studied. The ratio of the rate constants of reaction $1 + 2 \rightarrow 3$ in 1,2-dichloroethane and benzene, 6 : 1, is in good agreement with the data obtained earlier for other ene reactions [6]. Using the obtained data (Table 1), the rate constants in benzene at 25°C ($k_2 = 58.6 \text{ l mol}^{-1} \text{ s}^{-1}$), the activation enthalpy ($\Delta H^\ddagger = 20.0 \text{ kJ mol}^{-1}$), and the activation entropy ($\Delta S^\ddagger = -144 \text{ J mol}^{-1} \text{ K}^{-1}$) were calculated under the assumption that the reaction rate correlates with the rate-limiting step. Earlier, we determined these parameters for the ene reaction of **1** with cyclohexene in toluene ($k_2 = 7.99 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$; $\Delta H^\ddagger = 53.3 \text{ kJ mol}^{-1}$; $\Delta S^\ddagger = -106 \text{ J mol}^{-1} \text{ K}^{-1}$) and 1-hexene ($k_2 = 2.34 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$; $\Delta H^\ddagger = 51.8 \text{ kJ mol}^{-1}$; $\Delta S^\ddagger = -122 \text{ J mol}^{-1} \text{ K}^{-1}$). From these data, we may conclude that the main reason for the increased rate of reaction $1 + 2 \rightarrow 3$ relative to the ene reactions between **1** and 1-hexene and cyclohexene is the lower activation enthalpy ($\Delta\Delta H^\ddagger = -33.3$ and $-31.8 \text{ kJ mol}^{-1}$, respectively), despite the loss in activation entropy ($298\Delta\Delta S^\ddagger = 11.4$ and 6.6 kJ mol^{-1} , respectively). It was of interest to discover what determines the change in the rate of ene reaction of **1** in a series of alk-

Table 2. Ionization potentials of a series of alkenes (IP_{ad} , eV) and the rate constants of their reactions with triazolinedione **1** ($\ln k_2$ [$L \text{ mol}^{-1} \text{ s}^{-1}$]) in dichloromethane at 23.5°C

No.	Alkenes	IP_{ad}	$\ln k_2$
1	2,3-Dimethyl-2-butene	8.27	5.81*
2	2-Methyl-2-butene	8.68	1.87
3	<i>cis</i> -3-Hexene	8.95	-0.115
4	<i>cis</i> -2-Butene	9.11	-0.967
5	<i>trans</i> -2-Butene	9.10	-1.71
6	2-Methylpropene	9.24	-1.64
7	1-Hexene	9.46	-4.61
8	1-Methylcyclopentene	8.60	0.652
9	1-Methylcyclohexene	8.67	-0.641
10	<i>trans</i> -2,5-Dimethyl-3-hexene	8.84	-3.26
11	Cyclohexene	8.94	-2.99
12	Cyclopentene	9.01	-2.10
13	Norbornene	8.81	-7.26

* The data in this work are given for 1,2-dichloroethane.

enes. Data on the ionization potentials of alkenes (IP_{ad}) [7] and their reaction rate constants with triazolinedione **1** in dichloromethane [6] are presented in Table 2.



Dependence of the rate constant ($\ln k_2$) of ene reactions for a series of alkenes with 4-phenyl-1,2,4-triazoline-2,5-dione on their ionization potentials (IP_{ad}). The numbering of points corresponds to Table 2.

A clear increase in the rate of ene reaction on enhancement of their π -donor properties is observed only in the reaction with linear alkenes (nos. 1–7). For cycloalkenes and 1-methylcycloalkenes, a more complex dependence is observed in Fig. 1, due probably to the additional effect of the difference between the energies of C=C bonds in cycloalkenes (nos. 11–13) and the difference between the energies of endocyclic and exocyclic C=C bonds (nos. 8, 9).

CONCLUSIONS

The value of the equilibrium constant for the reaction **1** + **2** \rightarrow **3** can be estimated if the values of the entropy of activation and the entropy of reaction are comparable. The value of the equilibrium constant ($\sim 7 \times 10^{16} \text{ L mol}^{-1}$) obtained with these calculations allows us to consider the reaction **1** + **2** \rightarrow **3** as an irreversible process.

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