

Kinetics of 1,3-Cycloaddition of α -Diazoalkanones to Maleic Anhydride

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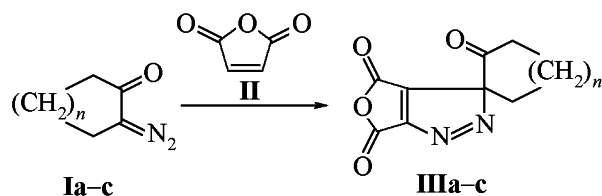
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Abstract—The kinetics of 1,3-cycloaddition to maleic anhydride were studied by examples of reaction with five-, six-, and seven-membered α -diazocycloalkanones. The order of magnitude of the thermodynamic activation parameters in the reaction series investigated corresponds to a concerted mechanism of the process under consideration.

Most published data on cycloaddition kinetics of diazoalkanes, mainly diazomethane, diphenyldiazomethane and its derivatives can be interpreted as following concerted mechanism of reaction [1]; however, in some cases the possibility of intermediate radicals formation cannot be excluded [2].

Kinetics of 1,3-cycloaddition of diazoalkanones was not treated before this study. We investigated the process by an example of reaction between diazo-cycloalkanones **Ia–c** with maleic anhydride (**II**).



$n = 1$ (a), 2 (b), 3 (c)

The choice of dipolarophile was due to the following reasons: The reactivity of α -diazocarbonyl

compounds was known to be lower than that of diazoalkanes [3, 4], therefore the second component of the cycloaddition should be sufficiently reactive dipolarophile; it was shown formerly [5] that among the derivatives of the ethylene series commonly applied to these processes the most reactive toward five-membered oxacyclic α -diazoketone was maleic anhydride (**II**).

For selection of kinetics measurement procedure we considered in detail the spectral characteristics of the initial compounds **Ia–c** (see the table) and of the final reaction products **IIIa–c** (for compounds **IIIa, b** see [6], for compound **IIIc** see EXPERIMENTAL).

In the UV spectra of diazoalkanes appear one or two maxima in the region 250–300 nm that should be assigned to π - π^* -transitions as show the high extinction and a red shift in going to a solvent of greater polarity. In the UV spectrum of anhydride **II** a strong maximum is observed in 220 nm region overlapping with the absorption maxima of diazoketones **Ia–c** that

Spectral characteristics and dipole moments of diazoketones **Ia–c**

Compd. no.	UV spectrum, λ_{\max} , nm (log ϵ)		IR spectrum, cm^{-1}		μ , D
	hexane	ethanol	N=N	C=O	
Ia	250 (4.05) 300 (3.03)	252 (4.70) 278 (3.92)	1345, 2093	1691	3.7 ± 0.1
Ib	267 (3.72)	281 (4.18)	1355, 2090	1635	4.1 ± 0.1
Ic	–	–	1342, 2086	1635	–

prevents the use of UV spectroscopy for kinetic measurements.

We registered the complete IR spectra of diazoalkanes **Ia–c** for the first time. The characteristic absorption bands of the stretching carbonyl vibrations are observed in the 1635–1690 cm^{-1} region. Two bands belong to the characteristic stretching vibrations of the diazo function: that of asymmetrical stretching vibrations at 2100 cm^{-1} , and another one at 1340 cm^{-1} , apparently that of symmetrical bending vibrations typical of triatomic systems with cumulated bonds [7]. The latter band is convenient for diazo group identification.

Just the IR method was chosen for kinetic measurements and evaluation of the thermodynamical activation parameters in the reaction series under investigation.

We showed previously [6] that the reaction between diazocycloalkanes **Ia, b** with maleic anhydride (**II**) gave rise to the corresponding Δ^1 -pyrazolines **IIIa, b**. The cycloaddition of diazocycloalkane **Ic** to anhydride **II** was not accomplished before. We established that this reaction at room temperature results in gradual tarring of the reaction mixture providing intractable products. When the reaction was carried out at 3–4°C for three days we succeeded in isolating of a product that we were able to purify.

The elemental analysis of the product thus isolated was consistent with the presumed composition of compound **IIIc**. Its structure is confirmed by the IR spectrum: a strong absorption at 1575 cm^{-1} may be ascribed to the stretching vibrations of the N=N bond, and two strong bands at 1811 and 1895 cm^{-1} apparently belong to the stretching vibrations of C=O group from the anhydride moiety whereas the absorption band at 1730 cm^{-1} corresponds to the stretching vibrations of C=O in the seven-membered ring [8]. In the ^1H NMR spectrum of compound **IIIb** appear two doublets from vicinal protons of the fused system. Thus the spectral characteristics confirm the adduct structure as Δ^1 -pyrazoline.

The kinetic measurements were carried out in dioxane at 10–45°C at 100-fold excess of maleic anhydride (**II**). The concentration of diazoalkanes **I–c** was measured from IR spectra. The slope of plots $\log \alpha$ was processed by least-squares procedure. The rate constants were calculated by formulas [9]:

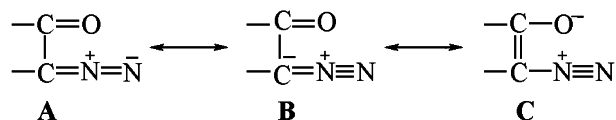
$$k_1 = -\tan a/0.434$$

$$\text{and } k_2 = k_1/c_{\text{II}}$$

From the plots $\log k_2 - 1/T$ were determined the thermodynamical activation parameters of the process [10]. Here are given compound nos, $k_2(30^\circ\text{C}) \times 10^4$ ($\text{l mol}^{-1} \text{s}^{-1}$), ΔH^\ddagger (kJ mol^{-1}), ΔS^\ddagger ($\text{J mol}^{-1}\text{-deg}^{-1}$): **Ia**, 16.8, 34 ± 3 , -186 ; **Ib**, 3.5, 55 ± 4 , -128 ; **Ic**, 4.9, 56 ± 4 , -123 .

The data obtained show far greater reactivity of diazoketone **Ia** compared with diazoketones **Ib, c**. Apparently this fact may be rationalized as follows: With the five-membered cyclic diazoketone intermediately arises more compact transition state convenient for cycloaddition where the most planar five-membered cycle provides a possibility of attack on the diazofunction from any side. With six-membered and seven-membered cyclic diazoketones the hydrocarbon part of the molecule is not planar and can hinder the approach of the dipolarophile.

The problem of charge distribution on the reaction center of the initial diazoketones may be treated with the use of mesomeric structures (A–C).



The spectral characteristics of the cyclic monoketones and diazoketones suggest that the largest statistical weight for compound **Ia** corresponds to the structure **B** whereas for **Ib** and **Ic** corresponds the structure **C**.

The dipole moments of diazocycloalkanes **Ia** and **Ib** measured by us (see the table) support this assumption: the smaller dipole moment of the diazocyclopentanone **Ia** more likely corresponds to the charge distribution in structure **B**, and the greater dipole moment of compound **Ib** is due to the stronger charge separation in the structure **C**.

The dipole of **B** type is obviously more favorable for cycloaddition, and that also is apparently consistent with the highest reactivity of diazoketone **Ia** in the series of diazocycloalkanes **Ia–c**.

The large negative value of ΔS^\ddagger corresponding to the process suggests an orderly cyclic structure of the transition state. It is also evidenced by relatively small positive values of ΔH^\ddagger [10].

Thus the order of magnitude of the activation parameters of the reaction series under study corresponds to the concerted mechanism of the process under consideration.

EXPERIMENTAL

UV spectra were recorded on spectrophotometer SF-46. IR spectra were registered on spectrophotometer UR-20 in CCl_4 ($c \sim 0.1 \text{ mol l}^{-1}$). ^1H NMR spectra were run on Varian HA-100 D-15 instrument (100 MHz from 10% solutions in CDCl_3 , internal reference TMS).

The diazocycloalkanones **Ia-c** were synthesized by diazotransfer reaction [11, 12]. The diazocycloalkanones **Ia-c** obtained were purified by column chromatography on neutral alumina of Brockmann II grade activity (eluent hexane-ethyl ether, 1:1). The final purification of diazoalkanones **Ia-c** was performed by vacuum distillation. The anhydride **II** was recrystallized from chloroform followed by vacuum sublimation.

Study of cycloaddition kinetics. The reaction was carried out in a closed cell maintained as constant temperature within 10–50°C range. Twice sublimed anhydride **II** was used in 100-fold excess. The concentration of diazo compounds **Ia-c** was monitored by measuring IR absorption on the band of stretching vibrations of the diazo group at 2100 cm^{-1} . With each compound were carried out five measurements at five different temperatures.

Anhydride of 6-oxo-1,2-diazospiro[4.6]undec-1-ene-3,4-dicarboxylic acid (IIIc). To a solution of 207 mg of diazocycloheptanone (**Ic**) in 1 ml of ethyl ether was added 147 mg of sublimed anhydride **II**. The mixture was left standing for 3 days at 3–4°C. The precipitated colorless crystals of compound **IIIc** were filtered off and purified by repeated washing with anhydrous ethyl ether. Yield 215 mg (60%), mp 89–90°C (decomp.). IR spectrum (1% solution in

CHCl_3 , cm^{-1}): 3060 v.w, 2960 m, 2885 w, 1895 s, 1811 v.s, 1730 s, 1575 w, 1475 m, 1260 m, 1093 v.s, 935 v.s. ^1H NMR spectrum, δ , ppm): 1.45–2.74 m (OH); 4.15 d (H); 6.07 d (H). Found, %: C 55.97; H 5.14; N 11.86. $\text{C}_{11}\text{H}_{12}\text{N}_2\text{O}_4$. Calculated, %: C 55.92; H 5.13; N 11.86.

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