311. Kinetic Investigation of a (6 + 4) Cycloaddition

by **Hiroshi Tanida** and **H. R. Pfaendler**

Shionogi Research Laboratory, Shionogi & Co., Ltd., Fukushima-ku, Osaka 553, Japan

(25. V. 72)

Summary. Kinetics of the [6+4] cycloaddition of tropone to cyclopenta-1,3-diene were investigated. It was concluded that the mechanism of this cycloaddition is similar to that of the classic *Diels-Alder* reaction.

Since the initial investigation of the addition of tropone to cyclopenta-1,3-diene [1], which was the first example of a [6 + 4] cycloaddition allowed by *Hoffmann* & *Woodward*'s analysis of the symmetry of the interacting orbitals [2], no, or only little information [3] has been obtained about the kinetic course of this reaction type. The main difficulties in obtaining kinetic data on [6 + 4] addition reactions of tropone are supposed to be the low stability of its adducts, which readily undergo a retro cycloaddition reaction [1] and also its sensitivity towards light and high temperatures. Furthermore the dienes themselves are easily dimerized.
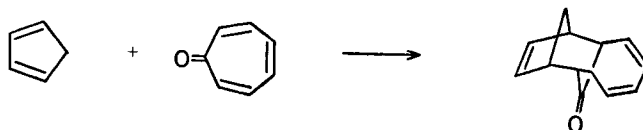
We report here a kinetic study of the addition of tropone to cyclopenta-1,3-diene, the most reactive and representative example of the [6 + 4] addition type. The above-mentioned difficulties, *i.e.* dimerisation of cyclopenta-1,3-diene and retro cycloaddition, could be overcome by using a large excess of tropone. Addition of a small amount of hydroquinone led to a clean reaction, which was easily followed by gas chromatography using the pseudo first order method [4]. As in our recent investigations of *Diels-Alder* reaction kinetics [5], dioxane proved to be a very suitable solvent. As shown in Fig. 1, a logarithmic plot against time of the ratio of the area of the cyclopenta-1,3-diene peak to that of an internal standard (cyclohexane) gave an excellent straight line. Experiments under similar conditions, using one reactant only, showed no dimerisation of cyclopenta-1,3-diene or tropone. A 77% yield of adduct, based on cyclopenta-1,3-diene, and the absence of significant amounts of other products were determined by gas chromatography. Table 1 shows the influence of temperature change and concentrations on the reactivity. Only a slight change of reactivity was observed even in the presence of higher concentrations of hydroquinone and, as expected, no effect of change in reactant concentrations was observed. The calculated activation enthalpy $\Delta H^{\pm}$ was found to be 15.3 kcal · mol^{-1} and the entropy change $\Delta S^{\pm} - 35$ e.u. at 100°. A logA value of 5.6 was obtained. Since a relatively small value of enthalpy and a high negative value of entropy change are common observations in classic [4 + 2] *Diels-Alder* reactions [6], the kinetic results
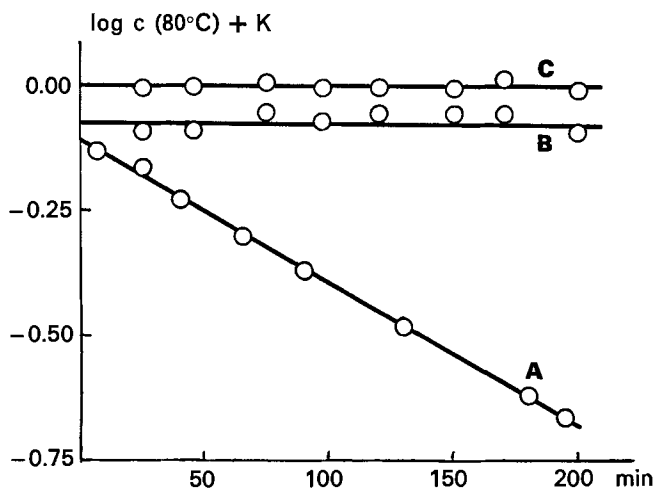
log c (80°C) + K

Fig. 1. *Determination of rate constants by the pseudo-first order method*

A: 2.0 M tropone and 0.1 M cyclopenta-1,3-diene

B: 2.0 M tropone

C: 0.1 M cyclopenta-1,3-diene

in dioxane containing 0.05 M hydroquinone

Table 1. *Effects of temperature and concentration on reaction rate*

Temperature (°C)	Concentrations (mol/l)			Obs. sec. ord. rate const. $(1 \cdot mol^{-1} \cdot sec^{-1})$
	Tropone	Cyclopentadiene	Hydroquinone	
40	2.0	0.1	0.05	$2.71 \cdot 10^{-6}$
60	2.0	0.1	0.05	$1.23 \cdot 10^{-5}$
80	2.0	0.1	0.05	$5.48 \cdot 10^{-5}$
	2.0	0.1	0.25	$6.39 \cdot 10^{-5}$
	1.0	0.05	0.05	$5.13 \cdot 10^{-5}$
100	2.0	0.1	0.05	$1.62 \cdot 10^{-4}$

are compatible with the idea that the reaction between tropone and cyclopentadiene is, from a mechanistic viewpoint, simply an example extended from the [4 + 2] cycloaddition.

Experimental

All concentrations are temperature corrected. Gas chromatographic studies were carried out on a *Hitachi* K 53 gas chromatograph, equipped with a flame ionisation detector. As constant temperature reactor, a *Haake* R 22 Thermostat with an accuracy of ± 0.05° was used. Physical properties are described in former publications [1].

Kinetics. Into each of eight 1 ml ampoules was put 0.1 ml of a freshly prepared solution containing tropone, cyclopenta-1,3-diene, hydroquinone and cyclohexane (internal standard) in pure dioxane. The ampoules were flushed with nitrogen at − 70°, sealed, then kept in a constant temperature bath. At appropriate time intervals during two half lives, one ampoule was removed from the bath, cooled in ice water to stop the reaction and its contents immediately injected into the gas chromatograph using a *Hitachi* R-45 Ucon oil LB-550 X (45 m) column at 25°. From the ratios of the areas of the cyclopentadiene peaks to those of the internal standard, the pseudo first

order rate constants were calculated by a computer program using the least square method. By dividing these values by the molar concentration of tropone, the appropriate second order rate constants were obtained.

A possible dimerisation of cyclopentadiene was investigated in the same way without using tropone in the reaction mixture. To investigate possible tropone dimerisation, a solution of tropone, hydroquinone and *n*-eicosane (internal standard) in pure dioxane was treated as above mentioned. In this case a 5% XE-60 chromosorb W (2 m) column was used together with a temperature program.

Yield determinations. Yields of adduct were determined similarly, after seven half lives, using a 1% OV-17 on chromosorb W (2 m) column at 150° and comparing the ratio of the area of the adduct peak to that of an internal standard (*n*-eicosane) with the ratio obtained from a test mixture of adduct m.p. 68° [1] and *n*-eicosane.

BIBLIOGRAPHY

[1] a) *R. C. Cookson, B. V. Drake, J. Hudec & A. Morrison*, Chem. Commun. *15* (1966); b) *S. Ito, Y. Fujise, T. Okuda & Y. Inoue*, Bull. chem. Soc. Japan *39*, 1351 (1966).

[2] *R. Hoffmann & R. B. Woodward*, Accounts Chem. Res. *1*, 15 (1968); *R. B. Woodward & R. Hoffmann*, 'The Conservation of Orbital Symmetry', p. 83–85, Verlag Chemie, GmbH-Academic Press Inc., Weinheim, 1970.

[3] *S. Ito, K. Sakan & Y. Fujise*, Tetrahedron Letters No. 10, 775 (1969).

[4] a) *T. Tsuji, S. Teratake & H. Tanida*, Bull. chem. Soc. Japan *42*, 2033 (1969); b) *R. Huisgen, F. Mietzsch, G. Boche & H. Seidl*, 'Organic Reaction Mechanisms', The Chemical Society, London, 1965, p. 3.

[5] *H. Tanida & H. R. Pfaendler*, unpublished results.

[6] *A. Wassermann*, 'Diels-Alder Reactions', p. 38–53, Elsevier Publishing Co., Amsterdam-London-New York, 1965; *A. A. Frost & R. G. Pearson*, 'Kinetics and Mechanism', p. 104–107, John Wiley and Sons, Inc., New York, N.Y. 1961.

Errata

Correction and Complementary Remarks

to

The 5,6-Dihydro-2H-pyran-2-ide Cyclopropyl-enolate Rearrangement

by V. Rautenstrauch

Research Laboratories, *Firmenich & Cie*, Geneva, Switzerland

We have reported [1] that lithiation of 5,6-dihydro-2*H*-pyran **7**[1]) with butyllithium/TMEDA gives the allylic carbanion **2**, together with the isomeric carbanion **14**, trapped as trimethylsilyl derivatives **13** and **15**, respectively. This is incorrect: in fact, only carbanion **2** is formed. The 60 MHz NMR. spectrum of **15** was misinterpreted [1][2]) and structure **15** is incorrect. The correct structure is **15a**. Like **13**, **15a** is

---

[1])   Numbering of formulae as in ref. [1].

[2])   I thank Dr. *J. F. Biellmann*, Université de Strasbourg, for pointing out this possibility.