ON THE THERMAL DECOMPOSITION OF PROPENE IN THE PRESENCE OF 1,3-BUTADIENE. THE ROLE OF DIELS-ALDER REACTION

By

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The thermal decomposition of propene in the presence of 1,3-butadiene was studied in the temperature range 745—809 K. 45 products were identified, and the initial rates of formation were determined from gas-chromatographic analysis of the products. It was concluded that radical chain processes and molecular reactions contribute to product formation.

From the initial rates of formation of 4-methylcyclohexene and toluene, the rate coefficient of the reaction

$$C_3H_6 + 1,3-C_4H_6 \rightarrow \text{4-methylcyclohexene}$$
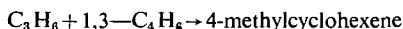
was determined as

$$\log (k_{DA}/dm^3\,mol^{-1}\,s^{-1}) = 7.74 \pm 0.29 - (129.3 \pm 6.1)\,kJ\,mol^{-1}/2.303\,RT$$

The results obtained support the concerted nature of the Diels—Alder reaction.

Introduction

Since some of the products of the thermal decompositions of olefins are more reactive than the parent compounds themselves, these products may influence even the formation of the major products. Thus, the roles of the different reaction paths in the formation of a given product may change considerably with increasing conversion.

In an attempt to clarify the routes of formation of some of the products of the thermal decomposition of propylene (P), the reaction was studied in the presence of different amounts of 1,3-butadiene (B).

The thermal decomposition of P has been studied under various experimental conditions (see e.g. [1—5]), whereas reaction of B has not been investigated so extensively [6—8]. In the reaction of P in the presence of B, the formation of aromatic products (benzene, toluene) was examined under industrial conditions [9—10]. The improvement of the analytical techniques made possible the identification of a great number of products, and an effort is made here and in a forthcoming publication to describe in more detail the effect of B on the pyrolysis of P.

P has long been known to inhibit the decomposition of many hydrocarbons. In the addition and abstraction reactions of both saturated alkyl radicals and H atoms, these species are converted into relatively less reactive radicals, decreasing the rates of

accumulation of different products. In the presence of **B**, a significant increase was expected in the overall rate of addition to **B**, since these reactions yield resonance-stabilized radicals and are essentially irreversible, while the similar reactions of **P** are not.

Experimental

Apparatus

The experiments were carried out in a conventional static system. Pyrex and quartz reaction vessels $0.146\,dm^3$ ($S/V = 0.114\,dm^{-1}$) and $0.139\,dm^3$ ($S/V = 0.109\,dm^{-1}$) in volume were used. The reaction temperature was kept constant within $\pm$ 0.5 K over the temperature range 745—809 K.

Mixtures of the reactants were prepared in a temperature-controlled spherical vessel. Efficient mixing was ensured by convection, brought about by warming a side-arm of the mixing vessel for two hours.

When **B** was decomposed alone, CO_2 diluent was used at nearly the same partial pressure as that of **P** in the **P**+**B** mixtures.

Pressure measurements were made with a precision pressure gauge (Texas Instruments, Inc.) in the range 0—80 kPa. The products of the reaction were expanded into a pyrex vessel containing a known amount of a gas standard (2-methyl-1-
-butene, FLUKA AG, 99.9% purity). The rest of the reaction mixture was frozen into $2.5 \cdot 10^{-4}\,dm^3$ solvent (decane, FLUKA AG, 99.9% purity, or *sec*-butylbenzene, 98% purity) containing a precisely measured internal standard (2,2,3,3-tetramethyl-butane, FLUKA AG, 99.9% purity).

The C_1—C_4 products were analyzed in the gas sample and the C_5—C_8 products in the solution.

Materials

The **P** (Tisza Chemical Works) and **B** (FLUKA AG) used in the experiments were of high purity. Both reactants were subjected to repeated low-temperature bulb-to-bulb distillation and were degassed before admission into the storage vessels. After this procedure the main impurities were 0.02% ethane+ethene and 0.13% propane in **P** (99.85% purity) and 0.49% C_5 olefins in **B** (99.51% purity).

The gas-chromatographic identifications were made with chemicals of high purity (FLUKA AG, 99.9% purity, and CHEMICAL SAMPLES, 99.9% purity).

Analysis

The reaction products were analyzed with Hewlett—Packard 5750G and 5734A gas-chromatographs equipped with FID. The quantitative analysis of the products was performed with a Hewlett—Packard 3380S integrator.

The C_1—C_4 products were separated on a Chromosorb P (80/100 mesh) column coated with 20% BMEA (bis(2-methoxyethyl)-adipate); column length: 6.1 m, $\varnothing$ 0.22 cm. The operating temperature was 298 K.

1-Butene and isobutene were separated on the former column connected to a Durapak column 0.9 m in length, with ∅ 0.22 cm. The operating temperature was 298 K. The carrier gas was N_2 and a flow rate of $2 \cdot 10^{-2}$ dm³ min⁻¹ was applied. These columns were purified by means of the "back flush" method at 353 K.

Ethane and ethene were separated at 363 K on an alumina column 1 m in length, while the C_5—C_8 compounds were analyzed on a DC—550 SCOT capillary column 30 m long, at 298—353 K. The flow rate of the carrier gas was $2.5 \cdot 10^{-3}$ dm³ min⁻¹ and the split ratio was 1/10. The analysis was not continued beyond the appearance of the peak of styrene since the combined area of the subsequent peaks amounted to less than 2% of the total peak area of all the other products.

The products were identified via retention times, Kovats retention indices [11], selective olefin and aromatic absorption [12] and mass-spectrometry (FINNIGAN 1015 S/L).

Results

Pressure measurements

Figure 1 shows the total pressure vs. time plots at different $[B]_o/[P]_o$ ratios. In the early stages of the reaction, the rate of negative pressure change increases with increasing $[B]_o$.

From the expression

$$- \frac{dp_T}{dt} = \text{const.} [B]_o^\beta$$

Fig. 1. Total pressure vs. time plots at $[P]_o = 2.93 \cdot 10^{-3}$ mol dm⁻³ at $[B]_o/[P]_o$ ratios of 1/99 (1), 1/74 (2), 1/49 (3), 1/19 (4), 1/9 (5) and 1/4 (6) at 793 K

where p_T is the pressure at temperature T, values of β (768 K) = 1.22 ± 0.04 and β (793 K) = 1.24 ± 0.06 were calculated at $[P]_o = 2.93 \cdot 10^{-3}$ mol dm⁻³, clearly indicating the role of B in the oligomerization processes.

Analytical results

The experiments were performed at ten different temperatures in the interval 745—908 K, while $[P]_0$ and $[B]_0$ were in the ranges $0 - 3.21 \cdot 10^{-3}$ mol dm⁻³ and $0 - 8.08 \cdot 10^{-4}$ mol dm⁻³, respectively. The conversion was 3.0—20.1% for P, and 1.3—68.0% for B.

In the analytical study of the pyrolysis of P in the presence of B, 45 products were identified. The identification results are summarized in Table I, where the products are listed according to decreasing rates of formation. Further, a comparison is given to specify the products identified in the detailed studies on P decomposition
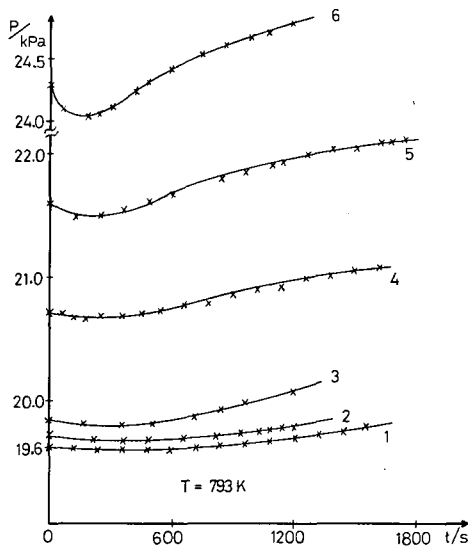
Table I

Identified products of the P + B reaction

Products	Method of identification [a]	Ref. [b] [8, 13, 14]
methane	GC	+
ethene	GC	+
1-butene	GC	+
t-2-butene	GC	+
c-2-butene	GC	+
cyclopentene	GC, MS	+
1,3-cyclopentadiene	GC, MS	+
4-methyl-1-pentene	GC, MS	+
3-methyl-1-pentene	GC, MS	+
c-1,3-pentadiene	GC	+
3-methylcyclopentene	GC, MS	+
4-methylcyclopentene	MS	
5-methyl-1,3-cyclopentadiene	MS	
1,4-cyclohexadiene	MS	
cyclohexene	GC, MS	
1,3-cyclohexadiene	GC, MS	
4-methylcyclohexene	GC, MS	+
hydrogen	GC	+
benzene	GC, MS	+
1-hexene	GC, MS	+
1,5-hexadiene	GC, MS	+
toluene	GC, MS	+
propane	GC	+
ethane	GC	+
3-methyl-1-butene	GC	+
1-pentene	GC, MS	+
1,4-pentadiene	GC	+
t-2-pentene	GC, MS	+
c-2-pentene	GC, MS	+
isobutene	GC	+
2-methyl-1,3-butadiene	GC, MS	+
C_5-olefin	MS	+
2-methyl-1-pentene	MS	
4-vinylcyclohexene	GC	
1-methyl-1,4-cyclohexadiene	GC	
ethylbenzene	MS	
1,3-dimethylbenzene	GC, MS	
1,2-dimethylbenzene	GC, MS	
styrene	MS	
2-methyl-1-butene	GC, MS	
2-methyl-2-pentene	GC, MS	+
1,3-hexadiene	GC	+
1-methylcyclopentene	GC, MS	+
1-methylcyclohexene	GC, MS	+
2-methyl-1,5-hexadiene	MS	

[a] GC: identification with gas-chromatography
   MS: identification with mass-spectrometry
[b] The sign + designates compounds identified in earlier investigations of the thermal decomposition of P [1, 13, 14].

by KALLEND et al. [1] and SIMON and BACK [13, 14]. The products of the **P**+**B** reaction are very similar to those of the **P** reaction under similar conditions. At high conversions of **P** in the reaction of the pure reactant, and also at higher $[B]_o/[P]_o$ ratios some further products appeared, but their combined amount was negligible.

The products can be classified into two groups, according to their accumulation patterns. The concentrations of some products continually increase throughout the reaction, while those of others reach maxima and subsequently decrease. Among the more important products of the first group are CH_4 (Fig. 2), C_2H_6, C_2H_4, C_3H_8, butenes, 5-methyl-1,3-cyclopentadiene, benzene (Fig. 3) and toluene, while those in the second group include cyclopentene + 1,3-cyclopentadiene, 1-hexene + 1,5-hexadiene (Fig. 4), cyclohexene + 1,3-cyclohexadiene (eluted together), 3- and 4-methyl-
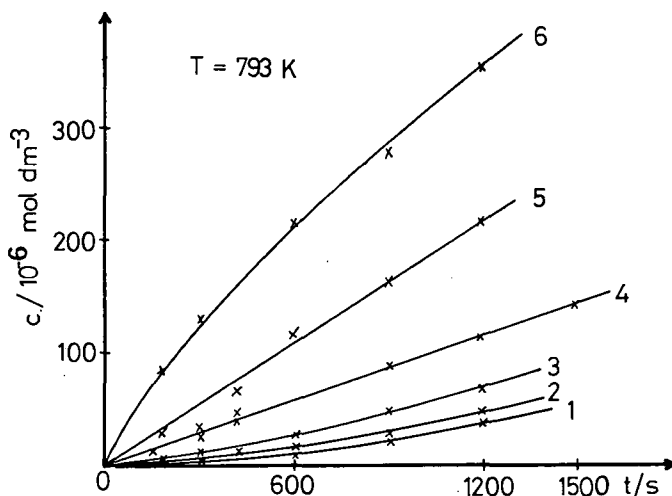

Fig. 2. Yields *vs.* time plots of methane at $[P]_o = 2.93 \cdot 10^{-3}$ mol dm^{-3} at $[B]_o/[P]_o$ ratios of 0 (1), 1/99 (2), 1/49 (3), 1/19 (4), 1/9 (5) and 1/4 (6) at 793 K

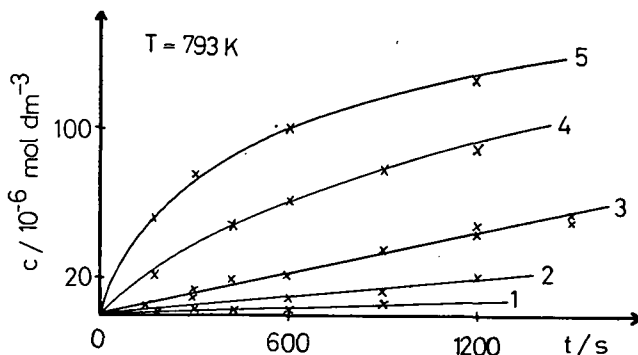*Fig. 3.* Yields *vs.* time plots of benzene at $[P]_o = 2.93 \cdot 10^{-3}$ mol dm^{-3} at $[B]_o/[P]_o$ ratios of 1/99 (1), 1/49 (2), 1/19 (3), 1/9 (4) and 1/4 (5) at 793 K

cyclopentenes, 4-methylcyclohexene (Figs. 5 and 6) and 1,4-cyclohexadiene. While the initial rates of product accumulations can be determined quite reliably for the first group of products, the values calculated for the second group are only semi-quantitative in nature. The amounts of allene and butane were too small to be detected in the present investigation. These products are formed in more substantial amounts in reactions carried out at higher temperatures [15, 16]. In contrast to the result obtained by BACK and SIMON [13, 14], 1-methyl-cyclopentene and 2-hexene were not found to be major products of the reaction of pure P. Similarly, 1,3-hexadiene and 1,4-hexadiene, identified as major reaction products by KALLEND et al. [1], were not found in our measurements. The shapes of the product accumulation curves indicate that some products (methane, ethene, butenes, cyclopentene + 1,3-cyclopentadiene, 3-and 4-methylcyclopentenes and cyclohexadienes) are formed mostly in secondary reactions in the reaction of pure P [1, 5, 13, 14]. With increase in [B]$_o$ these curves became more linear.

After the early stages of the reactions, the relative yields of the unsaturated C$_5$- and C$_6$-membered cyclic products increase.

The effect of B on the initial rates of formation of the products can be illustrated by the apparent reaction orders with respect to B. Table II contains these values for some important products at 748 and 793 K.
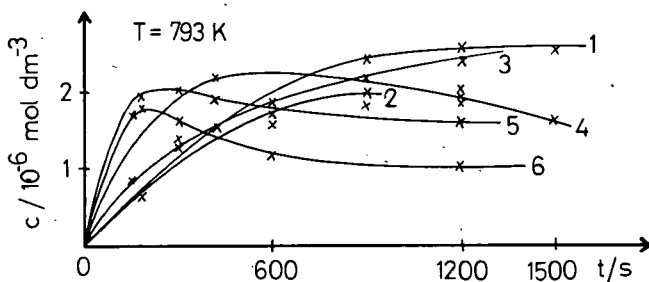

Fig. 4. Yield vs. time plots of 1-hexene + 1,5-hexadiene at
[P]$_o$ = 2.93 · 10^{-3} mol dm^{-3} at [B]$_o$/[P]$_o$ ratios of
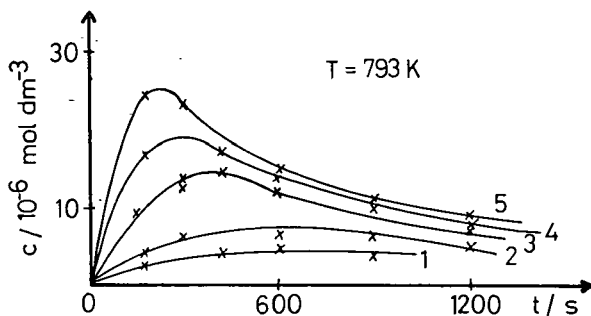0 (1), 1/99 (2), 1/49 (3), 1/19 (4), 1/9 (5) and 1/4 (6) at 793 K

Fig. 5. Yield vs. time plots of 4-methylcyclohexene at
[P]$_o$ = 2.93 · 10^{-3} mol dm^{-3} at [B]$_o$/[P]$_o$ ratios
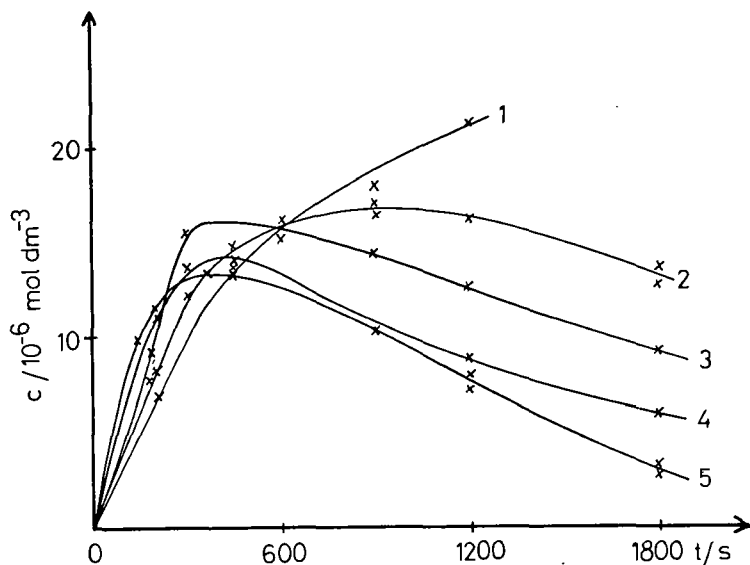of 1/99 (1), 1/49 (2), 1/19 (3), 1/9 (4) and 1/4 (5) at 793 K

Fig. 6. Yields *vs.* time plots of 4-methylcyclohexene at
$[P]_o = 2.93 \cdot 10^{-3}$ mol dm^{-3}, $[B]_o = 1.56 \cdot 10^{-3}$ mol dm^{-3} at
753 K (1), 768 K (2), 775 K (3), 782 K (4) and 793 K (5)

Table II

The apparent order of formation of some products with respect to **B** *at 768 and 793 K*

| T/K	768	793
methane	0.96 ± 0.07	0.96 ± 0.04
ethane	0.96 ± 0.04	1.06 ± 0.07
ethene	0.90 ± 0.05	0.94 ± 0.05
1-butene	1.05 ± 0.12	0.97 ± 0.09
t-2-butene	0.88 ± 0.08	0.98 ± 0.07
c-2-butene	0.93 ± 0.07	0.94 ± 0.10
cyclopentene	1.10 ± 0.06	0.90 ± 0.05
1,3-cyclopentadiene		
1-hexene	0.49 ± 0.07	0.28 ± 0.10
1,5-hexadiene		
3-methylcyclopentene	0.62 ± 0.04	0.57 ± 0.02
4-methylcyclopentene	0.60 ± 0.04	0.21 ± 0.02
cyclohexene	1.17 ± 0.08	1.06 ± 0.10
1,3-cyclohexadiene		
1,4-cyclohexadiene	1.38 ± 0.09	1.22 ± 0.11
benzene	1.22 ± 0.12	1.16 ± 0.09
4-methylcyclohexene	0.90 ± 0.07	0.51 ± 0.07
toluene	1.58 ± 0.06	1.49 ± 0.07
cC_6—R cyclic compounds [a]	1.11 ± 0.05	1.05 ± 0.07
toluene + 4-methylcychlohexene	1.04 ± 0.09	0.97 ± 0.06

[a] $R \equiv H$ or CH_3.

Since there are no predominant oligomeric products of the reactions (a number of major products are formed in similar quantities), the **P** + **B** reaction seems to be a rather complicated process. In spite of this, the apparent order of reaction for **B** is nearly unity (within narrow error limits) for most of the compounds (listed in Table II). **B** is apparently a common precursor of most of the products, even in the thermal decomposition of pure **P**.

Discussion

As will be demonstrated below, reactions of both radical chain and molecular characters are involved in the thermal decomposition of **P** in the presence of **B**. Since the order of reaction with respect to **B** was found to be close to unity for most of the products, the two kinds of processes must exhibit a similar dependence on $[B]_0$. An attempt is made below to clarify the role of molecular processes. Other aspects of the reaction will be discussed elsewhere.

As concluded earlier, **B** is obviously a precursor of most of the products formed, if even moderate amounts of **B** are added to **P** initially. The large amounts of methane, ethene, ethane and some other products clearly indicate that radical processes are of major importance in the overall reaction.

It is well known, however, that molecular processes of the Diels—Alder (DA) [17] and ene reaction types [18] are common in systems similar to ours. These processes may yield some of the products observed in our system in a straightforward manner and may be the predominant source of these compounds. The major DA reaction in the B-influenced reaction of **P** is

$$B \; + \; P \; \longrightarrow \; \text{[cyclohexene ring with methyl group]} \qquad (1)$$
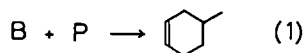
Since the products (4-methylcyclohexene (4MCH), methylcyclohexadienes (MCHD) and toluene (T) formed from 4MCH) of this reaction sequence are present in negligible concentrations in the early stages of the reaction, the reaction is irreversible at $t \approx 0$, and so reaction (1) is rate-determining. The products formed *via* the DA reaction might also be formed in radical reactions *via* addition of radical **A** to **B**, *e.g.*

$$B \; + \; A \longrightarrow \text{[cyclohexene ring]} \longrightarrow \text{products} \qquad (2)$$
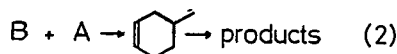
A: allyl radical

If the kinetic role of reaction (2) in the formation of 4MCH and T is not negligible, the Arrhenius parameters calculated from the initial rates of accumulation of these products are too low.

The rate coefficient of the DA reaction was calculated from the equation

$$k_{DA} = \frac{r_o(4MCH) + r_o(T)}{[P]_o[B]_o}$$

Table III

Experimentally determined rate constants of **P** + **B** *DA reaction*

T/K	$\dfrac{[P]_o}{10^{-3}\,M^{a}}$	$\dfrac{[B]_o}{10^{-4}\,M}$	$\dfrac{r_o(4MCH)+r_o(T)}{10^{-9}\,M\,s^{-1}}$	$\dfrac{k_{DA}}{M^{-1}s^{-1}}$	$\dfrac{\bar{k}_{DA,T}\pm\sigma^{b}}{M^{-1}s^{-1}}$
753	2.93	0.296	3.017	0.03479	0.05655 ± 0.03077
753	2.93	1.56	35.79	0.07831	
761	2.93	0.296	6.202	0.07151	0.08221 ± 0.01513
761	2.93	1.56	42.47	0.09291	
768	2.56	0.523	11.12	0.08309	
768	2.56	2.85	77.09	0.1057	
768	2.56	6.44	137.5	0.08341	
768	2.93	0.296	7.156	0.08251	
768	2.93	0.602	15.03	0.08521	
768	2.93	1.56	52.33	0.1145	0.09246 ± 0.01891
768	2.93	3.29	121.6	0.1260	
768	2.93	7.37	172.8	0.08002	
768	3.21	0.655	14.48	0.06889	
768	3.21	3.57	129.9	0.1133	
768	3.21	8.08	193.0	0.07443	
775	2.93	0.296	8.155	0.09402	0.1126 ± 0.02629
775	2.93	1.56	59.96	0.1312	
782	2.93	0.296	10.05	0.1158	0.1275 ± 0.01648
782	2.93	1.56	63.59	0.1391	
788	2.93	0.296	14.21	0.1638	0.1640 ± 0.000282
788	2.93	1.56	75.03	0.1642	
793	2.56	0.523	28.70	0.2144	
793	2.56	2.85	133.4	0.1829	
793	2.56	6.44	256.9	0.1558	
793	2.93	0.296	16.30	0.1880	
793	2.93	0.399	15.07	0.1289	0.1586 ± 0.02781
793	2.93	0.602	23.99	0.1360	
793	2.93	3.29	142.0	0.1473	
793	2.93	7.37	297.1	0.1376	
793	3.21	3.57	167.7	0.1463	
793	3.21	8.08	340.2	0.1312	
801	2.93	0.296	18.95	0.2185	0.2185 ± 0.02^{c}
809	2.93	0.296	21.68	0.2500	0.2500 ± 0.02^{c}

ᵃ $M = mol\,dm^{-3}$
ᵇ $\bar{k}_{DA,T}$ = the mean value of k_{DA} at the temperature T, σ = standard deviation
ᶜ standard deviation estimated

The calculated rate coefficients are shown in Table III. Finally, the Arrhenius expression for k_{DA} calculated from the exponential form of the Arrhenius equation is

$$\log(k_{DA}/dm^3\,mol^{-1}\,s^{-1}) = (7.74 \pm 0.28) - (129.3 \pm 6.1)kJ\,mol^{-1}/2,303\,RT$$

where the indicated uncertainties represent one standard deviation of the mean values of the parameters. (The weighting factor was $1/\sigma_i^2$).

A comparison of the parameters obtained with those determined for similar reactions (Table IV) shows reasonable agreement, although our data seem to be on the high side. We also conclude that these parameters are high enough to support our assumption concerning the negligible contribution of radical reactions.

Table IV

*Arrhenius parameters of some DA reactions of B*

Diene	Dienophile	T/K	$\log(A/dm^3\,mol^{-1}\,s^{-1})$	$E/kJ\,mol^{-1}$	Ref.
B	ethene	760—921	7.48	115.1	[23]
B	P	900—1150	7.40	122.7	a
		753—809	7.74 ± 0.28	129.3 ± 6.1	this work
B	B	464—557	6.95	102.6	[6]
		446—660	6.95	99.2	[24]
		691—923	8.14	112.2	[23]

^{a} Calculated from equilibrium constant obtained from thermochemical calculations (data in Table V) using the rate constant of the retro—DA reaction [20].

Table V

Thermochemical data used in the calculations [52, 26]

Compounds	$\Delta H^0_{f,\,298\,K}/kJ\,mol^{-1}$	$S^0_{298}/J\,mol^{-1}\,K^{-1}$	$C_p/J\,mol^{-1}\,K^{-1}$			
			$a\cdot10$	$b\cdot10^2$	$c\cdot10^6$	$d\cdot10^9$
P	20.42	266.94	50.895	22.560	-99.873	13.283
B	110.16	278.74	-163.03	41.339	-342.38	114.92
4-methyl-cyclohexene	-33.372	355.11	-627.24	77.921	-521.73	136.82

The mechanism of the DA reaction and thus the retro-DA reaction is still under discussion. The thermal decompositions of many C_3 and C_4 rings are accepted as occurring by a biradical mechanism [19], and those of C_6 rings by a concerted mechanism. The decomposition of 4-vinylcyclohexene [20] the DA adduct of **B** (formed in our system, too), is considered to be a biradical process made possible by the formation of two relatively stable allylic radical centres [21]. Our experimentally determined activation energy for the DA reaction between **P** and **B** appears to confirm the concerted mechanism of this reaction, in disagreement with the results of SAKAI et al. [22]. A plausible biradical route would be:

$$\bigcirc \overset{a}{\underset{-a}{\rightleftharpoons}} \bigcirc \overset{b}{\underset{-b}{\rightleftharpoons}} B \;+\; P \qquad (3)$$
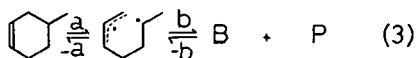
$\Delta H^0_{f,\,793K}/kJ\,mol^{-1}$ -64.4 ~253 102.2   23.0

The heat of formation of the biradical was estimated following the argumentation used by BENSON [21]. The corrections used in the estimation were twice a half 1,5H-repulsions, one *cis*, and two alkene gauche corrections. The structure of this adduct was assumed to be similar to a C_6 ring, with E_{-a} about 0—4 kJ mol^{-1}. Starting from the thermochemical data (see also Table V), $\Delta H^0_{a,\,793\,K}$ is 317.4 kJ mol^{-1}. For the activation energy of reaction a

$$E_{a,\,calc.} > \Delta H^0_{a,\,793} + E_{-a} \cong 317.4\,kJ\,mol^{-1}$$

obtained by the calculations above, and

$$E_a = 285.4 \text{ kJ mol}^{-1}$$

from the present work and the calculated equilibrium constants. The difference is about 32 kJ mol^{-1}, supporting the concerted mechanism.

Acknowledgements

The authors are indebted to Miss M. Markovits for her technical assistance.

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ТЕРМИЧЕСКИЙ РАСПАД ПРОПЕНА В ПРИСУТСТВИИ 1,3 БУТАДИЕНА РОЛЬ РЕАКЦИИ ДИЛЬСА-АЛДЕРА

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Изучен термический распад пропена в присутствии 1,3 бутадиена в интервале температур 745—809 К. Идентифицировано 45 соединений и установлены начальные скорости их образования на основании данных газо-хроматографического анализа. Образование продуктов проходит как радикально-цепным, так и молекулярным механизмом. Полученные результаты подтверждают концертную природу реакции Дильса-Алдера.