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Kinetics of the Diels–Alder Addition of Acrolein to Cyclohexa-1,3-diene and Its Reverse Reaction in the Gas Phase

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Abstract

The Diels–Alder addition of acrolein to cyclohexa-1,3-diene has been studied between 486 and 571°K at pressures ranging from 55 to 240 torr. The products are endo- and exo-5-formylbicyclo[2.2.2]oct-2-ene (endo- and exo-FBO), and their formations are second order. The rate constants (in l./mole·sec) are given by

$$\log_{10} k_{\text{endo}} = -(19{,}470 \pm 50)/4.576T + (5.65 \pm 0.02)$$

$$\log_{10} k_{\text{exo}} = -(20{,}630 \pm 50)/4.576T + (5.51 \pm 0.02)$$

The retro-Diels–Alder pyrolysis of endo-FBO has also been studied. In the ranges of 565–638°K and 6–38 torr, the reaction is first order, and its rate constant (in sec^{-1}) is given by

$$\log_{10} k_p = -(46{,}390 \pm 110)/4.576T + (12.98 \pm 0.04)$$

The reaction mechanism is discussed. The heat of formation and the entropy of endo-FBO are estimated.

Introduction

The kinetics and the mechanism of the gas-phase Diels–Alder reaction

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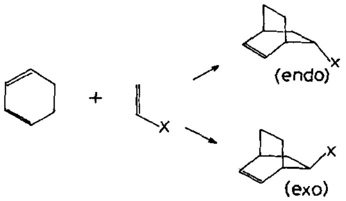

and of its reverse have been recently studied for X = CH_3 [1,2]. This paper deals with the case where X = CHO.

Experimental

Cyclohexa-1,3-diene (Chd) was as in [1]. Acrolein (A) (Merck) was distilled under vacuum to a purity better than 99.4%. A mixture of endo- and exo-5-formylbicyclo[2.2.2]oct-2-ene (endo- and exo-FBO, respectively) was obtained by condensation of Chd with A in an autoclave [3]. After vacuum distillation, the mixture of the two isomers contained less than 0.2% impurity, and the endo- to exo-FBO ratio En/Ex was 90/10 ($n_D^{18} = 1.5003$ and $T_f = 12.1°\mathrm{C}$ compared to 1.4990 [4], and 12–13°C [5], respectively). A few small samples of mixtures with En/Ex ranging from 97/3 to 45/55 were obtained after several consecutive gas chromatographic separations on 250-μl samples of the 90/10 mixture. A 2-m column (inner diameter 0.5 cm) containing 30% by weight of tricresylphosphate on 45–60 mesh Chromosorb P was used. The temperature was 130°C and the hydrogen flow rate 7 l./hr. The endo- and exo-structures of the two FBO isomers were deduced from the position of the carbonyl proton in the nuclear magnetic resonance spectra [6]; the molecular weight was 136 as determined by mass spectrometry, and the infrared spectrum showed the typical absorptions of the carbonyl group and of bicyclo[2.2.2]oct-2-ene [7].

The kinetic apparatus has been described elsewhere [8]. The reactions were followed by measuring the variation of the total pressure and by analyzing the products by gas chromatography. The sampling technique was as in [2], and the analyses were carried out with a katharometer in the same gas chromatographic conditions as those given above. No "seasoning" of the reaction cells was needed to obtain reproducible results. The reaction percentages were always kept lower than 2%.

Results

Addition of Acrolein to Cyclohexa-1,3-diene

The reactions of acrolein (A) with cyclohexa-1,3-diene (Chd) have been studied between 486 and 571°K. The pressures of both reactants were varied from 25 to 130 torr. The products are the Diels–Alder adducts endo- and exo-5-formylbicyclo[2.2.2]oct-2-ene[1] (endo- and exo-FBO, respectively). Their rates of formation can be represented by

$$v_{\mathrm{en}} = d(\text{endo-FBO})/dt = k_{\mathrm{en}}(\mathrm{Chd})(\mathrm{A}) \tag{2}$$

and

$$v_{\mathrm{ex}} = d(\text{exo-FBO})/dt = k_{\mathrm{ex}}(\mathrm{Chd})(\mathrm{A}) \tag{3}$$

and do not depend on the surface-to-volume ratio S/V of the reaction cell (see

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[1] Small amounts of other products are also formed but were shown to result from the thermal reactions of Chd alone [1,2].

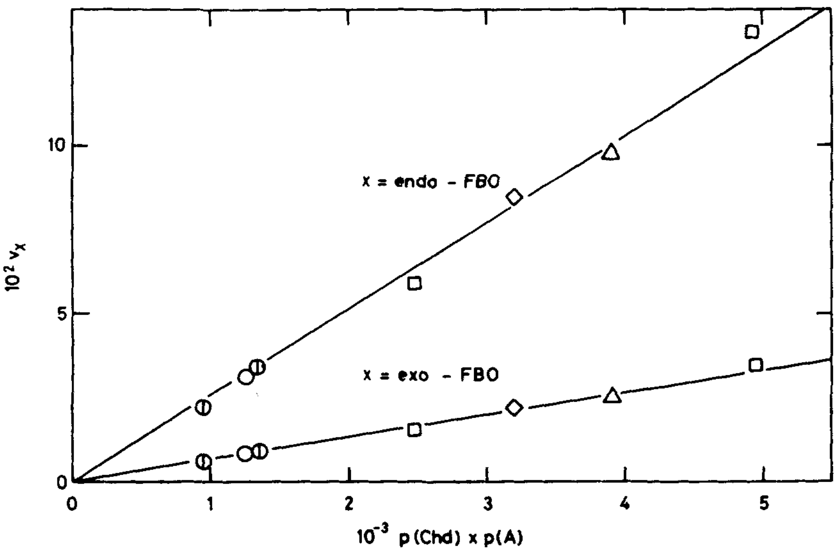


Figure 1. Addition of A to Chd at $\bar{T} = 569.6°K$. Dependence of the rates of formation v (torr/min) of endo- and exo-FBO on the pressures of Chd and A (torr). Reaction cell with $S/V = 1.2 \text{ cm}^{-1}$: ○, □, △, ◇—$p$(Chd) = 25, 50, 75, 100 torr, respectively; reaction cell with $S/V = 9.0 \text{ cm}^{-1}$: ⦶—p(Chd) = 25 torr.

Fig. 1). Figure 2 shows Arrhenius plots of the rate constants k_{en} and k_{ex} (in l./mole·sec). Least mean square treatment of their values gives

$$\log_{10} k_{en} = -(19{,}470 \pm 50)/4.576T + (5.65 \pm 0.02) \tag{4}$$

and

$$\log_{10} k_{ex} = -(20{,}630 \pm 50)/4.576T + (5.51 \pm 0.02) \tag{5}$$

where the limits are for one standard deviation.

Pyrolysis of 5-formylbicyclo[2.2.2]oct-2-ene (FBO)

The pyrolysis of mixtures of 90% endo- and 10% exo-FBO has been studied between 565 and 638°K at pressures ranging from 6 to 28 torr. The reaction proceeds with an increase of the total pressure equal to the partial pressures of the Chd and A formed. No products other than those expected for a retro-Diels–Alder reaction are formed. The initial rate v_p of total pressure increase is first order with respect to the total pressure P of FBO and is unaffected when 10 torr of propene is added to the reaction mixture. An Arrhenius plot of the

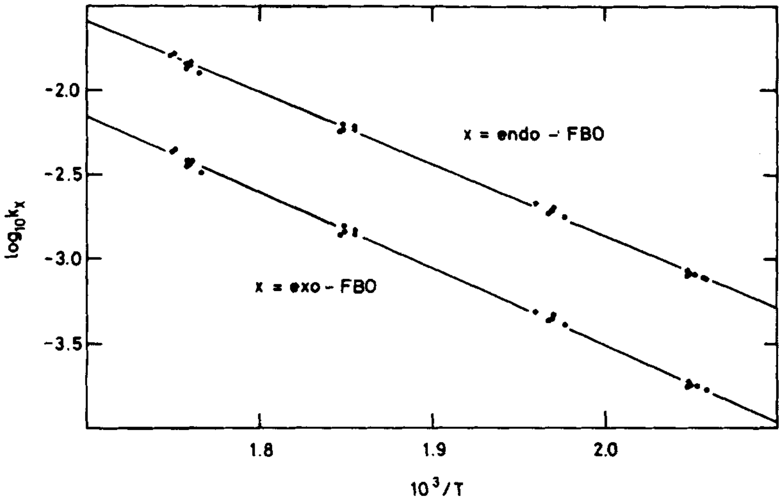


Figure 2. Addition of A to Chd. Arrhenius plot of k_{en} and k_{ex} (l./mole·sec). T—absolute temperature. Straight lines obtained by least squares.

rate constant $k_p = v_p/P$ (in sec^{-1}) is shown in Figure 3. Least mean square treatment of the values of k_p gives

$$(6) \qquad \log_{10} k_p = -(46{,}390 \pm 110)/4.576T + (12.98 \pm 0.04)$$

where the limits are for one standard deviation. A few experiments have shown that the value of k_p is unaffected when the endo-/exo-FBO ratio (En/Ex) of the reaction mixture is varied from 97/3 to 45/55. The values of the rate constants for the pyrolyses of the endo- and exo-isomers must therefore be similar and close to that given by eq. (6). However, as this equation was obtained from mixtures containing 9 times more endo- than exo-FBO, it will be used later only for the pyrolysis of endo-FBO. The experiments with the highest En/Ex ratios also show that endo-FBO isomerizes to exo-FBO with a rate constant k_i about 2.4 times smaller than k_p.

Discussion

The reaction of A with Chd is a Diels–Alder addition yielding endo- and exo-FBO and the pyrolysis of endo-FBO is a reverse Diels–Alder decomposition to A and Chd. Combining the Arrhenius parameters for the formation and decomposition of endo-FBO [see eqs. (4) and (6), respectively] enables one to calculate the heat of reaction $\Delta H°$ and the entropy change $\Delta S°$ of the reaction A + Chd $\rightarrow$ endo-FBO at about 560°K. The results are $\Delta H°_{560} = -28.04$ kcal/mole and $\Delta S°_{560} = -43.14$ gibbs/mole, where the standard state is the ideal gas at one atmosphere. From these values, using heats of formation $\Delta H°_{f,298}$,

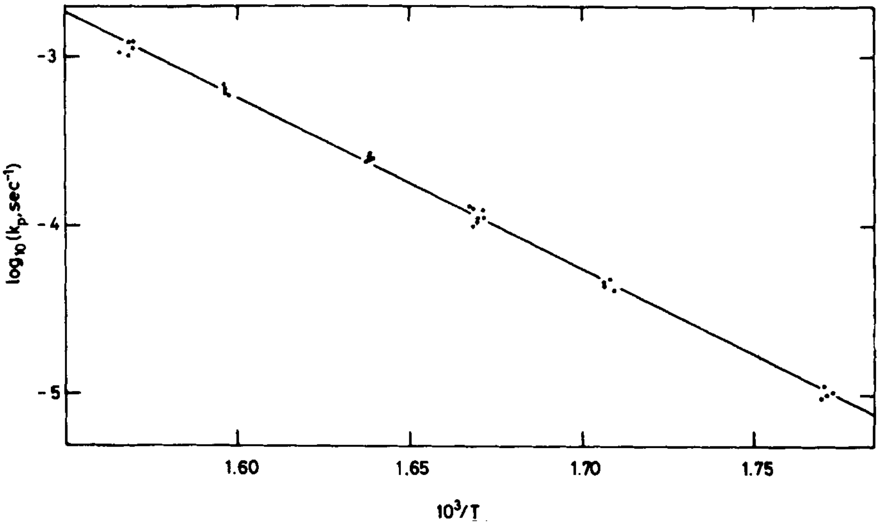
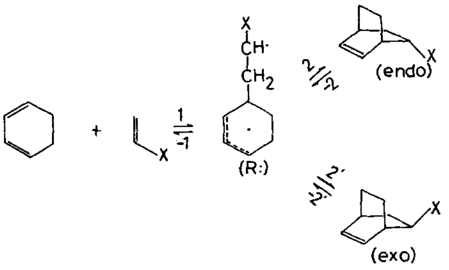


Figure 3. Pyrolysis of mixtures of 90% endo- and 10% exo-FBO. Arrhenius plot of k_p. T—absolute temperature. Straight lines obtained by least squares.

entropies $S°_{298}$, and heat capacities $C°_p$ given in Table I, one calculates $\Delta H°_{f,298}$ (endo-FBO) = −19.5 kcal/mole and $S°_{298}$ (endo-FBO) = 97.9 gibbs/mole. These values are comparable with $\Delta H°_{f,298}$ (FBO)[2] = −19.4 kcal/mole obtained from group additivities [9] and $S°_{298}$ (FBO) = 96.5 gibbs/mole estimated by the difference method [10] (for details see the legend for Table I). The values of the Arrhenius parameters for the formation of endo- and exo-FBO and the decomposition of endo-FBO are compared in Table II with those observed for endo- and exo-5-methylbicyclo[2.2.2]oct-2-ene (endo- and exo-MBO) [1,2]. As can be seen, substituting a CH_3 group by a CHO group leads to a lowering of both the activation energies and the preexponential factors, the net result being an increase of the reaction rates by a factor of about 200 at 600°K.

The following biradical mechanism

(7)



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[2] The abbreviation FBO is used when no distinction is made between the endo- and exo-somers.

TABLE I. Heats of formation ΔH°_f (in kcal/mole), heat capacities C°_p, and entropies (in gibbs/mole), based on 1-atm standard state.

Compounds	$\Delta H^\circ_{f,298}$	$C^\circ_{p,300}$	$C^\circ_{p,400}$	$C^\circ_{p,500}$	$C^\circ_{p,600}$	$C^\circ_{p,700}$	S°_{298}
Chd	25.9[a]	23.8[a]	31.1[a]	37.3[a]	43.1[a]	47.7[b]	72.3[a] (σ=1, n=1)
A	-17.7[c]	16.1[d]	19.7[e]	23.0[d]	25.7[e]	27.9[d]	68.0[f] (σ=1, n=1)
FBO	-19.4[g]	35.4[h]	49.4[h]	61.3[h]	71.7[h]	80.0[b]	96.5[h] (σ=1, n=2)
R:	25.8[i]	40.3[j]	53.0[j]	63.7[j]	72.1[j]	81.1[b]	104.6[j,k] (σ=1, n=2)

σ—total symmetry number; n—number of optical isomers.

[a] Debande and Huybrechts [1].

[b] Extrapolated value.

[c] Obtained from group additivities [9].

[d] Smith [11].

[e] Interpolated value.

[f] Estimated by means of the model compound method [12] using buta-1,3-diene (B) (S°_{298} (B) = 66.6 gibbs/mole [13]) as model and correcting for the symmetry difference between B and A.

[g] Obtained from group additivities [9] using two alkane gauche corrections and a ring strain energy equal to that of bicyclo[2.2.2]oct-2-ene (11.1 kcal/mole) [2].

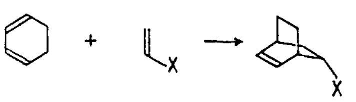
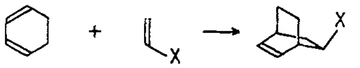
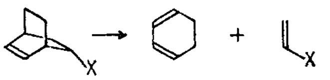
[h] Estimated by means of the model compound method [12] using 5-vinylbicyclo[2.2.2]-oct-2-ene (VBO) as model. The values for VBO were estimated by means of the difference method [10] starting with the values for 2-vinyl-1,4-dimethylcyclohexane obtained from group additivities [9] and using a ring tightness equal to that estimated for norbornene [10]. The values for the C°_p were corrected with the differences between the values for $CH_3—CH{=}CH_2$ and $CH_3—CHO$ [13].

[i] Obtained from group additivities [9] using a ring strain energy equal to that of cyclohexene [9]. The value for the additivity group CO–(C·)(H) was assigned equal to that for CO–(C)(H) [9] and the value for ·C–(CO)(C)(H) was that from [14], less a carbonyl resonance energy of 8.7 kcal/mole [14,15].

[j] Mean of the values for $—CH_2—\dot{C}H—CHO$ (less three vibrational contributions for an H atom in a C–H bond) and $—CH_2—\dot{C}H—CHO$ (plus three vibrational contributions for an H atom in a C–H bond). These values were estimated by means of the difference method [10] starting with the values for $—CH_2—\dot{C}H—CHO$ obtained from a combination of the values for $—CH_2—\dot{C}H—CH{=}CH_2$ estimated from group additivities [9], and the differences between the values for $CH_3—CH{=}CH_2$ and $CH_3—CHO$ [13].

[k] A correction of $-R \ln 2$ has been made for the difference between the electronic degeneracies of the singlet diradical R: and the doublet radicals used as estimation models.

TABLE II. Comparison of calculated activation energies (in kcal/mole) and preexponential factors A (in l.·mole·sec units) with experiments.

Reactions	E (exptl)	E (calc)	$\log_{10} A$ (exptl)	$\log_{10} A$ (calc)	Reference
 X = CH_3	26.1	26.1	5.7	6.3	(1)
X = CHO	19.5	19.2	5.6	5.6	this work
 X = CH_3	30.1	30.1	6.7	6.3	(1)
X = CHO	20.6	19.2	5.5	5.6	this work
 X = CH_3	56.0	56.2	14.2	14.7	(2)
X = CHO	46.4	46.1	13.0	12.9	this work

with X = CH_3 has recently been shown to be consistent with the experimental results for the Diels–Alder addition of propene to Chd and its reverse reaction [1,2]. This mechanism will now be tested in the case where X = CHO. Application of the steady-state treatment for initial conditions leads to the rate equations

$$v_{en} = d(\text{endo-FBO})/dt = (k_1k_2/xk_{-1})(\text{Chd})(\text{A}) \tag{8}$$

$$v_{ex} = d(\text{exo-FBO})/dt = (k_1k_{2'}/xk_{-1})(\text{Chd})(\text{A}) \tag{9}$$

$$v_p = -d(\text{endo-FBO})/dt = (k_{-2}/x)(\text{endo-FBO}) \tag{10}$$

where

$$x = 1 + (k_2/k_{-1}) + (k_{2'}/k_{-1}) \tag{11}$$

Equations (8)–(10) are of the same form as the experimental equations. Within the temperature range studied, the formation of endo-FBO is 4.2 ± 0.4 times faster than that of exo-FBO, and the decomposition of endo-FBO is about 2.4 times faster than its isomerization to exo-FBO. This implies that $k_2 \simeq 4.2\ k_{2'}$ and $k_{-1} \simeq 2.4\ k_{2'}$, respectively. Hence eq. (11) may be reduced to a good approximation to $x = 3.2$. Taking this into account as well as eqs. (8)–(10), the Arrhenius parameters for the reactions are

$$E_{en} = E_1 + E_2 - E_{-1}, \qquad E_{ex} = E_1 + E_{2'} - E_{-1}, \qquad E_p = E_{-2}$$

$$A_{en} = A_1A_2/3.2\ A_{-1}, \qquad A_{ex} = A_1A_{2'}/3.2\ A_{-1}, \qquad A_p = A_{-2}/3.2$$

These activation energies and preexponential factors have been calculated using the thermochemical data given in Table I and the same procedures and assumptions[3] as in the case where X = CH_3 [1,2]. Table II lists the calculated and experimental values. As for the case where X = CH_3, the agreement is very satisfactory. The lower values for the activation energy and frequency factor of the pyrolysis of endo-FBO compared with those for endo-MBO are explicable mainly in terms of the stabilization energy S and the loss of rotation of the formyl group of the biradical R:, respectively. The value used in this work for S, namely, 8.7 kcal/mole, was obtained from a diradical analysis [14] of the decomposition of formylcyclobutane [16]. This value is comparable with those for alkylacetonyl radicals resulting from diradical analyses of the isomerizations of acetylcyclopropane (ca. 7 kcal/mole) [17] and the decompositions of carbonyl-substituted cyclobutanes (7.7 ± 2 kcal/mole) [14]. These values for alkylacetonyl radicals are, however, larger than those obtained by halogen atom techniques for the methylacetonyl radical (2.7 kcal/mole) [18] and the unsubstituted acetonyl radical (0 kcal/mole) [19,20], which are in dispute [17,21]. Taking this into account it is not excluded that the value of S could be lower than 8.7 kcal/mole. In this case the calculated values of the activation energies for the reactions endo-FBO $\rightleftarrows$ Chd + A would be higher than the experimental values (Table II) so that these reactions would then probably be concerted.

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[3] The ring closings (2) and (2′) are assumed to have no activation energies ($E_2 = E_{2'} = 0$ kcal/mole) and the entropies of their transition states are set equal to that of the biradical R:, less the entropy associated with the free rotation of an ethyl group [14,15].

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