The Kinetics of Reversible Diels–Alder Reactions in the Gas Phase. Part II.[1] Cyclopentadiene and Ethylene

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The title reaction has been investigated in both directions in a static system. At temperatures in the range 521—570 K the addition of ethylene to cyclopentadiene (CPD) results in the formation solely of norbornene (NB) and the decomposition of the latter produces only ethylene and CPD. In a vessel of high surface : volume ratio, small quantities of nortricyclene are formed heterogenously. Kinetic studies support second and first orders for the addition and decomposition respectively. The mechanism $C_2H_4 + CPD \underset{1}{\overset{-1}{\rightleftharpoons}} NB$ is almost certainly homogeneous and molecular in nature. Least means squares analysis of the data yields equations (i) and (ii). Equilibrium

$$\log(k_1/s^{-1}) = (14.26 \pm 0.28) - (44.54 \pm 0.72 \text{ kcal mol}^{-1})/RT\ln10 \qquad \text{(i)}$$

$$\log(k_1/\text{l mol}^{-1}\text{ s}^{-1}) = (7.59 \pm 0.63) - (23.67 \pm 1.56 \text{ kcal mol}^{-1})/RT\ln10 \qquad \text{(ii)}$$

studies suggest that, for the addition, these Arrhenius parameters may be slightly high. Higher temperature investigations on this system (at equilibrium) indicate that no significant homogeneous molecular isomerisation of NB occurs with an activation energy < *ca.* 54 kcal mol^{-1}.†

As part of our continuing interest [1,2] in the thermodynamic properties of cyclic and polycyclic hydrocarbons, we were led to investigate equilibria involving norbornene (NB). Only an approximate value of the entropy of NB is listed [3] and there is disagreement over its heat of formation between values of 24.7 [4] and 15.1 kcal mol^{-1}.[5] Previously equilibrium data for norbornadiene have been obtained by study of the kinetics of its Diels–Alder reaction of formation as well as of its decomposition.[1] This technique is extended here to norbornene. The unimolecular decomposition has been studied before [6,7] and is only repeated as a check. The Diels–Alder formation kinetics have not previously been investigated. The study of systems which came to thermal equilibrium has potential spin-off. At higher temperatures the system will degrade chemically by an alternative route. Thus kinetic information may be obtained about a pathway other than the lowest, for one of the species present.

EXPERIMENTAL

Apparatus and *Experimental and Analytical Procedures*.—These were as described earlier.[1] A 2.5 m × 3 mm column of 15% w/w silicone oil on 60—80 Chromosorb P operated at 50° with N_2 carrier gas at an inlet pressure of 103 N m^{-2} was used for routine analysis. Calibration of the detector gave a response factor of 1.37 ± 0.02 for equal quantities of NB to cyclopentadiene (CPD).

Materials.—NB (Ralph Emanuel) was 99.5% pure. CPD was prepared and purified as previously [1] from dicyclopentadiene (BDH). Ethylene (Matheson C.P. grade) contained no other impurities detectable by g.l.c. and was not further purified.

RESULTS

(A) *Decomposition of Norbornene*.—Because the addition of CPD to ethylene was found to be reversible in preliminary experiments (*i.e.* substantial quantities of CPD were present at equilibrium under the conditions of addition experiments) the decomposition kinetics of NB were reinvestigated. The reaction vessel was the same as that used in an earlier study [1] and was not conditioned other than by preliminary experiments. A typical set of data is shown in Table 1. All data gave a good fit to an integrated first-order rate equation (at conversions up to 80%). The rate constants obtained from these plots were unaffected by pressure in the range 2—16 Torr. The reaction was studied at each of six different temperatures and the rate constants, k_1, are shown in Table 2.

TABLE 1

Product formation as a function of time in NB decomposition ($[NB]_0$ 4.6 Torr, T 531.35 K)

t/min	5	15	30	45	60	90	120
CPD (%)	2.7	7.7	14.5	21.0	27.3	37.0	46.0

TABLE 2

T/K	529.75	531.20	544.35	552.95	562.85	570.05
10^4k_1/s^{-1}	0.776 *	0.854	2.34	4.91	9.38	14.84

* Obtained in the packed vessel.

An Arrhenius plot of these constants gave equation (1).

$$\log(k_1/s^{-1}) = (14.26 \pm 0.28) - (44.54 \pm 0.72 \text{ kcal mol}^{-1})/RT\ln 10 \qquad (1)$$

The error limits quoted correspond to one standard deviation (68% confidence level) in the least-squares fit. The packed vessel run corresponding to the lowest temperature studied

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† 1 cal = 4.184 J.

[1] Part I, R. Walsh and J. M. Wells, *Internat. J. Chem. Kinetics*, 1975, **7**, 319.

[2] R. Walsh and J. M. Wells, *J. Chem. Thermodynamics*, 1975, **7**, 149.

[3] H. E. O'Neal and S. W. Benson, *J. Chem. and Eng. Data*, 1970, **15**, 266.

[4] R. B. Turner, P. Goebel, B. J. Mallon, W. von E. Doering, J. F. Coburn, and M. Pomerantz, *J. Amer. Chem. Soc.*, 1968, **90**, 4315.

[5] H. K. Hall, C. D. Smith, and J. H. Baldt, *J. Amer. Chem. Soc.*, 1973, **95**, 3197.

[6] W. C. Herndon, W. B. Cooper, and M. J. Chambers, *J. Phys. Chem.*, 1964, **68**, 2016.

[7] B. C. Roquitte, *J. Phys. Chem.*, 1965, **69**, 1351.

fits well with the other constants, and removes any suspicion of a heterogeneous process.

At long times (>60% conversion) small amounts of a side product (⩽3% of NB) were observed. Comparison with an authentic sample on two chromatographic columns showed the product to be nortricyclene.

(B) *Reaction of Cyclopentadiene with Ethylene.*—In this study ethylene was always kept in large excess so that the course of reaction was essentially indicated by CPD conversion into NB. Again at long times and particularly in the packed vessel small quantities of nortricyclene were found. However, under conditions where rates were measured nortricyclene formation was negligible.

To obtain a general idea of the time evolution of NB formation a series of runs was performed at each of four starting pressures of ethylene, in which the ratio [NB] : [CPD] was measured at various times until it became constant in value (presumably equilibrium). The results of these experiments are shown in Figure 1. It is clear that both the rate and steady-state value of the ratio increase with ethylene pressure in a roughly proportional way. To test these data further the ratio was fitted to the integrated reversible first-order rate equation and reasonably linear plots were obtained, at each pressure of ethylene. Thus a reaction first-order in both reactants is strongly indicated, *viz.* (2). In

$$\mathrm{CPD} + \mathrm{C_2H_4} \underset{1}{\overset{-1}{\rightleftharpoons}} \mathrm{NB} \qquad (2)$$

order further to substantiate the orders and to obtain k_{-1}, a series of runs was undertaken at a variety of starting pressures at each of five temperatures in which $k_1 + k_{-1}[C_2H_4]$ was obtained. This was done *via* the relationship $k_1 + k_{-1}[C_2H_4] = t^{-1} \ln [x_e/(x_e - x)]$ where x is the fraction of norbornene formed at time t, and x_e at equilibrium. In order to evaluate this expression it was necessary to know the

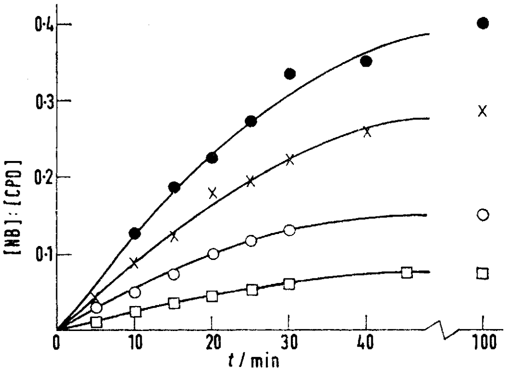

FIGURE 1 Product formation as a function of time at 553 K. Ethylene starting pressures/Torr: ●, 487; ×, 332; ○, 206; □, 99

TABLE 3

The equilibrium constant $K = [C_2H_4][CPD]/[NB]$

T/K	531.2	544.35	552.95	562.85	570.05	584.15	588.35
K/atm	0.51	0.87	1.25	1.87	2.43	4.25	5.19

equilibrium constant K. This was obtained independently during this study and although details are presented elsewhere,[8] for completeness the values are given in Table 3.

The quantity $k_1 + k_{-1}[C_2H_4]$ was then plotted against $[C_2H_4]$ at each temperature. Figure 2 shows an example of such a plot. Reasonably linear fits were obtained although with some scatter. In order to obtain k_{-1}, the slope of such a plot, the line was constrained to pass through an intercept corresponding to a value of k_1 determined from the decomposition. The precision of the k_{-1} values depended on the relative magnitudes of k_1 and $k_{-1}[C_2H_4]$ and in practice they were not easy to obtain to better than ±10%. In order to try to reduce the dependence of k_{-1} on both x_e and k_1, the lines obtained from these plots were weighted towards those points corresponding to low conversions but high ethylene pressures. The rate constants, k_{-1}, so obtained are shown in Table 4. Shown also for comparison purposes are values of k_{-1} calculated from the relationship $k_{-1} = k_1/K$. The agreement is reasonable, and although the 'experimental' values of k_{-1} depend to some extent on both k_1 and K they have been obtained by a different method than simply taking the ratio. The data obtained in the packed vessel are consistent with those in the unpacked vessel ($k_1 + k_{-1}[C_2H_4]$ values within 3%) at 531 K, and there is therefore no reason to suspect any heterogeneous contribution to the rate. At long times however, nortricyclene formation was once again observed, it being more significant in the packed than in the unpacked vessel. For this reason conversions were limited to below 40% (of equilibrium) where this side process was negligible.

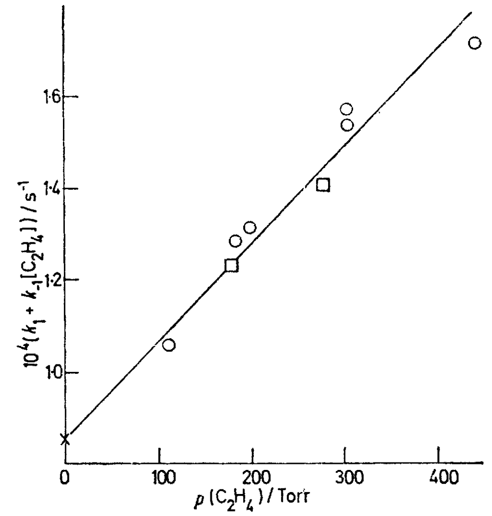

FIGURE 2 Apparent first-order rate constants as a function of ethylene pressure at 531 K: ○, unpacked vessel; □, packed vessel; ×, k_1 from NB decomposition

TABLE 4

T/K	10^4k_{-1}/atm^{-1} s^{-1}	$10^4k_1K^{-1}$/atm^{-1} s^{-1}
521.25	1.05 ± 0.20	
531.20	1.61 ± 0.14 *	1.68
544.35	2.74 ± 0.30	2.70
552.95	3.23 ± 0.48	3.93
562.85	5.68 ± 0.42	5.02
570.05		6.11

* Based on data part of which was obtained in the packed vessel.

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[8] R. Walsh and J. M. Wells, *J. Chem. Thermodynamics*, in the press.

An Arrhenius plot of the 'experimental' k_{-1} values in Table 4 gave equations (3) and (4) where the error limits

$$\log(k_{-1}/\text{atm}^{-1}\ \text{s}^{-1}) = (5.49 \pm 0.63) - (22.60 \pm 1.56\ \text{kcal mol}^{-1})/RT \ln 10 \quad (3)$$

$$\log(k_{-1}/\text{l mol}^{-1}\ \text{s}^{-1}) = (7.59 \pm 0.63) - (23.67 \pm 1.56\ \text{kcal mol}^{-1})/RT \ln 10 \quad (4)$$

correspond to one standard deviation in the least-squares fit.

In addition to these experiments some runs were performed in the temperature range 600—700 K. Under these conditions equilibrium quantities of NB were formed essentially instantaneously. At the high temperatures (>650 K) very complicated product chromatograms result. Apart from some formation of low boiling hydrocarbons such as ethane and propene, at least five products (two of which are major) with b.p.s. comparable with NB result. This complexity almost certainly means that radical pathways are involved, and as the purpose of these experiments was to discover whether a molecular pathway occurred, they were not pursued further and the products not characterised although certain compounds such as the methylcyclohexadienes were eliminated. However, on the assumption of pseudo-first-order kinetics (rate constant, k) for formation of the two major products from CPD in the presence of excess of C_2H_4 (*ca.* 490 Torr) equation (5) was derived (from data at 610, 635, 666, and 699 K).

$$\log(k/\text{s}^{-1}) = 5.26 - 29.5\ \text{kcal mol}^{-1}/RT \ln 10 \quad (5)$$

DISCUSSION

A comparison with previous work of Arrhenius parameters and rate constants for the norbornene decomposition is shown in Table 5. The Arrhenius parameters are in tolerable agreement but of the rate constants in the middle of our temperature range ours and Roquitte's [7] are in good agreement while that of Herndon and his co-workers [6] are significantly higher. It should be noted that these last workers' temperature range of study was considerably higher and this rate constant is an extrapolated value. Discrepancies of a similar magnitude were found in our previous study [1] and it can only be assumed that experimental errors are often larger than claimed.

TABLE 5

T/K	log (A_1/s^{-1})	E_1/ kcal mol^{-1}	10^4k/s^{-1} at 553 K	Ref.
577—716	13.78	42.75	7.67	6
539—577	13.85	43.47	4.68	7
521—570	14.28	44.54	4.76	This work

The mechanism of this retro-Diels–Alder reaction is undoubtedly concerted as was that for norbornadiene [1] and we are in agreement with the recent analysis of Benson and O'Neal.[9]

The kinetics of the addition reaction have not previously been investigated. The experimental Arrhenius parameters may be judged in two ways. First they may be compared with those calculated from a combination of k_1 and K; this latter yields equation (6).

$$\log(k_1\ K^{-1}/\text{l mol}^{-1}\ \text{s}^{-1}) = (6.42 \pm 0.28) - (20.77 \pm 0.72\ \text{kcal mol}^{-1})/RT \ln 10 \quad (6)$$

Thus although the agreement in absolute rate constant values is good there is some distortion in the Arrhenius plot leading to a discrepancy in parameters. The difficulty of obtaining the k_{-1} values and their inherent imprecision leads us to favour parameters closer to the above calculated ones although there may be slight distortions in the temperature dependence of k_1 and K as well. Some evidence for the latter is indicated in our discussion of the thermodynamics of this reaction.[8] Thus we favour the Arrhenius equation (7).

$$\log(k_{-1}/\text{l mol}^{-1}\ \text{s}^{-1}) \simeq 6.9 - 21.9\ \text{kcal mol}^{-1}/RT \ln 10 \quad (7)$$

Secondly the A factor may be judged in the light of Transition State Theory. This is clearly within the reasonable range of 10^6—10^8 l mol^{-1} s^{-1} observed for other concerted Diels–Alder processes.[1] It is of interest to compare this rate constant with that obtained [1] for acetylene addition to cyclopentadiene, *viz.* (8). For

$$\log(k/\text{l mol}^{-1}\ \text{s}^{-1}) = 7.51 - 24.19\ \text{kcal mol}^{-1}/RT \ln 10 \quad (8)$$

these two additions both A and E are comparable and the small differences which do exist are unlikely to be attributable to any simple effect. It has been noted previously [10] that for CPD, the rate of addition to carbon–carbon double bonds exceeds that to triple bonds (at room temperature). Our data offers the most straightforward possible comparison of this type and in fact supports this contention (at a typical reaction temperature of 553 K, relative rate constants are in the ratio 1.92; at room temperature this ratio would be higher). Recent theoretical work [11,12] points to the idea, originally expressed by Woodward and Katz,[13] that the Diels–Alder reaction, while concerted, occurs in two stages. Bond formation is envisaged as occuring sequentially although not as completely separately as implied by a biradical intermediate. It would, therefore, seem reasonable that a parallel should exist with radical addition to π systems, which clearly can only occur at one site. In this respect it is interesting to note that rate constants for methyl radical addition to both ethylene and acetylene are very comparable at experimental temperatures.[14] In the opinion of Kerr and Parsonage,[14] the preferred rate constant for addition to ethylene exceeds that for addition to acetylene by a factor of 1.3 at 437 K, although the combined uncertainties in the rate constants may well exceed this factor. In the past correlations have been

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[9] H. E. O'Neal and S. W. Benson, *Internat. J. Chem. Kinetics*, 1970, **2**, 423; NSRDS–NBS Bulletin No. 21, National Bureau of Standards, Washington, 1970, p. 336.

[10] P. Beltrame, 'Comprehensive Chemical Kinetics,' eds. C. H. Bamford and C. F. H. Tipper, Elsevier, Amsterdam, 1972, vol. 9, ch. 2, p. 87.

[11] M. J. S. Dewar, A. C. Griffin, and S. Kirschner, *J. Amer. Chem. Soc.*, 1974, **96**, 2225.

[12] J. W. McIver, *J. Amer. Chem. Soc.*, 1972, **94**, 4782.

[13] R. B. Woodward and T. Katz, *Tetrahedron*, 1959, **5**, 70.

[14] J. A. Kerr and M. J. Parsonage, 'Evaluated Kinetic Data On Gas Phase Addition Reactions,' Butterworths, London, 1972.

obtained between reactivity and some kind of π bond index.[15] In this case the thermochemical π bond energy[16] of ethylene is less than that of acetylene[17] which is in accord with the idea of the reactions with the latter being more difficult, but it is doubtful that this has any significance in view of the small size of the differences in rate.

The high temperature pyrolysis of the equilibrium mixture of C_2H_4, CPD, and NB, as mentioned leads to a product complexity suggestive of a radical reaction. Although the products were not identified and the kinetics not established, nevertheless on the assumption of product formation from *either* C_2H_4 + CPD *or* NB one may set limits to the occurence of bimolecular or unimolecular non-radical pathways. By use of the equilibrium constant for NB formation, the Arrhenius data for high temperature product formation indicate that no molecular pathway from NB can occur with a rate constant in excess of that given by $\log (k/\text{s}^{-1}) = 15.4 - 54.3$ kcal $\text{mol}^{-1}/RT \ln 10$. This result is not in conflict with thermochemical calculations[18] which suggest that, were they to be formed, the molecular products should be methyl cyclohexadienes [formed in a sequence involving prior isomerisation to bicyclo[4.1.0]hept-2-ene, with a rate constant given by $\log (k/\text{s}^{-1}) = 14.7 - 58$ kcal $\text{mol}^{-1}/RT \ln 10$]. Although in this reaction no other molecular product is found, such an approach may be more profitable in other systems.

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[15] For a review, see for example W. C. Herndon, *Chem. Rev.*, 1972, **72**, 157.

[16] S. W. Benson, ' Thermochemical Kinetics,' Wiley, New York, 1968, p. 50.

[17] D. M. Golden and S. W. Benson, *Chem. Rev.*, 1969, **69**, 125.

[18] R. Walsh, unpublished results.