



and temperature variations during a run, were within  $\pm 0.1$  K.

**Product Analysis.**—RW and RS both experienced considerable difficulty in g.l.c. analysis of mixtures of 4CP, PD, and HCl. Recombination of PD and HCl tended to occur during handling, and decomposition and *cis-trans* isomerisation of 4CP occurred readily, especially on metal surfaces. Hydrogen chloride caused problems, and no completely satisfactory method was found for its removal.

For quantitative g.l.c., RW condensed the whole reaction mixture into a bulb fitted with a Rotaflo tap and a Suba-seal cap coated internally with Araldite epoxy resin to reduce absorption into the rubber. After condensing in a fixed amount of hexane standard the mixture was evaporated, brought up to atmospheric pressure with air or nitrogen, and allowed to homogenise for 1.5–2 h, and 0.5 cm<sup>3</sup> portions were injected with a Pressure-Lok gas syringe into a Pye–Unicam 104 chromatograph with dual heated flame-ionisation detectors. The column was 3 m 10 wt. % Apiezon L on 80–100 mesh silanised Celite at 70 °C, and was additionally treated *in situ* with hexamethyldisilazane before use. Calibration plots of peak height ratio against pressure ratio for 4CP–hexane and *trans*-PD–hexane were linear and reproducible and synthetic mixtures were satisfactorily analysed. RW did not analyse for HCl, and since the above column did not separate *cis*- and *trans*-4CP completely, they measured the combined pressure of 4CP, assuming equal calibration factors for the two isomers.

RS expanded reaction mixtures through a heated line into a heated Dohrmann-Loenco L-208-8 stainless steel sampling valve with a 0.15 cm<sup>3</sup> sample loop, for direct injection into a 2.5 m column of 10 wt. % dinonyl phthalate plus 2.5 wt. % polyethylene glycol adipate at 75 °C. Decomposition of 4CP occurred if mixtures were left in the steel valve for any length of time; since the injection pressure was measured on the transducer trace, the contact time could be reduced to an acceptable period of *ca.* 2 s. Peaks were integrated with an Infotronics CRS-104, and calibration plots of peak area against pressure injected were reproducible and linear. Analyses of synthetic mixtures containing no HCl were correct within 5%, but when HCl was present the errors were as large as 20%. The best results were obtained by passing the products through a 2 cm tube containing urea on Celite prior to entering the sampling valve and g.l.c. column; the errors were then generally <10%. *cis*- and *trans*-4CP were fairly well separated on this column, but since pure samples of the individual isomers were not available, a mixture was used for calibration and the calibration factors were assumed equal. Analysis for HCl was achieved by condensing the reaction products into acetone (10 cm<sup>3</sup>) at 77 K, and titrating portions (1 cm<sup>3</sup>) of the resulting solution with 5mM-NaOEt in ethanol with lacmoid as indicator. This procedure gave good results with known amounts of HCl, and negligibly small titres with 4CP.

**Materials.**—*cis*- and *trans*-penta-1,3-diene (PD) (Fluorchem) and *trans*-but-2-ene (Matheson) were pure by g.l.c. and i.r. spectroscopy. 4-Chloropent-2-ene, prepared by addition of HCl to PD<sup>7</sup> and purified by repeated distillation through a 25 cm Poddelniak column, had b.p. 374–375 or

<sup>7</sup> E. A. Vdovtsova, *J. Gen. Chem. U.S.S.R.*, 1961, **31**, 95.

<sup>8</sup> D. F. Ewing and K. A. W. Parry, *J. Chem. Soc. (B)*, 1970, 970.

<sup>9</sup> H. M. Frey, A. M. Lamont, and R. Walsh, *J. Chem. Soc. (A)*, 1971, 2642; W. M. Marley and P. M. Jeffers, *J. Phys. Chem.*, 1975, **79**, 2085; 1976, **80**, 778.

375–376 K (lit.,<sup>7</sup> 375 K) (Found: C, 57.6; H, 8.3. Calc. for C<sub>5</sub>H<sub>9</sub>Cl: C, 57.4; H, 8.6%). G.l.c. of this material gave two peaks with height ratio 15:85 (RW) or area ratio 10:90(RS), and the n.m.r. spectrum showed two sets of peaks with a similar area ratio, in good agreement with the spectra reported for *cis*- and *trans*-4CP respectively.<sup>8</sup> Repeated attempts by both RW and RS to separate these isomers by preparative g.l.c. were unsuccessful; re-injection of the collected fractions gave virtually the same peak ratio as the original mixture, and it appears that interconversion of the two isomers occurs rapidly when they are condensed or exposed to metal surfaces (see also Results section).

## RESULTS

The pyrolysis of 4-chloropent-2-ene (4CP) in clean vessels was very fast and irreproducible, with rates decreasing as a carbonaceous deposit was formed on the glass walls. The ageing process was slow, however; and vessels were more successfully seasoned by several overnight pyrolyses of allyl chloride (100–200 mmHg) at 630 K. Provided no trace of air entered the vessel, the reaction was then reproducible.

The products of pyrolysis of 4CP were HCl (identified by i.r. and mass spectrometry and by titration) and penta-1,3-diene (PD) (identified by mass spectrometry and retention time on various g.l.c. columns). The PD was mainly *trans*, with varying small amounts of *cis*; the isomers were partially interconvertible under the reaction conditions<sup>9</sup> and the ratio was not studied in detail. The reaction under study thus appeared to be (1). In accordance with this equation, the ratio of final to initial pressure was nearly two over most of the accessible temperature range (mean and s.d. of mean 1.93<sub>3</sub> ± 0.01<sub>0</sub> for RW at 572–608 K and 1.92<sub>8</sub> ± 0.00<sub>3</sub> for RS at 583–602 K); the difference from 2.00 is attributable to the dead-space in the apparatus.<sup>10</sup> At temperatures below 550 K, the decomposition of *trans*-4CP was too slow to be followed to completion in a reasonable time, while above 610 K the pressure began to fall again at long times, and higher boiling products were observed on the g.l.c. These effects are attributed to Diels–Alder reactions involving PD, which reacts even on its own at such temperatures.<sup>11</sup>

The stoichiometry was checked in more detail by analysis of reaction mixtures and correlation of the results with the pressure change (Figure 1). Although the g.l.c. results of RS are rather scattered (as expected from analysis of synthetic mixtures) they serve as general confirmation of the very good agreement obtained from the other analyses. It would have been instructive to analyse separately for *cis*- and *trans*-4CP, in order to confirm unambiguously that the initial fast pressure change (see below) is due to rapid decomposition of the *cis*-isomer. The sampling technique of RW failed completely in this respect, the *cis:trans* peak height ratio being the same for 4CP recovered at any stage of the reaction. Using the direct-injection system of RS, with <5 s elapsing between termination of the reaction and injection to the g.l.c., a marked depletion of the *cis*-4CP was noted. *cis*-Concentrations of <1% of the remaining 4CP were recorded after the initial fast pressure change was complete, although the ratio returned to the 'normal'

<sup>10</sup> (a) P. J. Robinson, *Trans. Faraday Soc.*, 1965, **61**, 1655. (b) P. J. Robinson and G. G. Skelhorne, *J.C.S. Faraday I*, to be submitted.

<sup>11</sup> J. A. Berson, P. B. Dervan, R. Malherbe, and J. A. Jenkins, *J. Amer. Chem. Soc.*, 1976, **98**, 5937; compare also buta-1,3-diene, G. Huybrechts, L. Luykx, Th. Vandenboom, and B. Van Mele, *Internat. J. Chem. Kinetics*, 1977, **9**, 283.

10% if the gas mixture was left in the glass line for even a few minutes. There is thus direct and semiquantitative

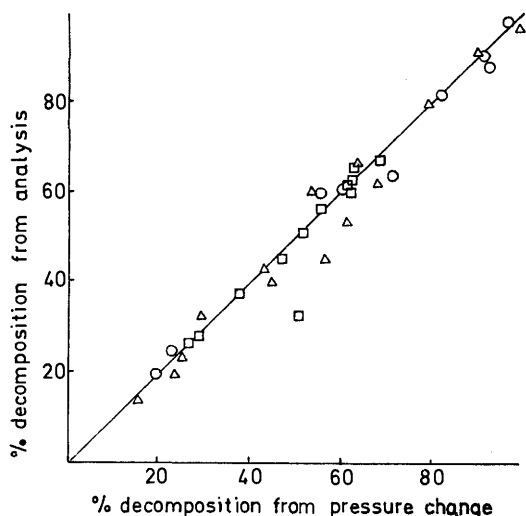


FIGURE 1 Demonstration of stoichiometry and comparison of analysis with pressure change. Percentage decomposition by analysis is obtained from HCl analysis by RS at 527–590 K (○) or g.l.c. determination of  $100/(1 + [4CP]/[PD])$  by RS at 574–594 K (△) and RW at 560–627 K (□)

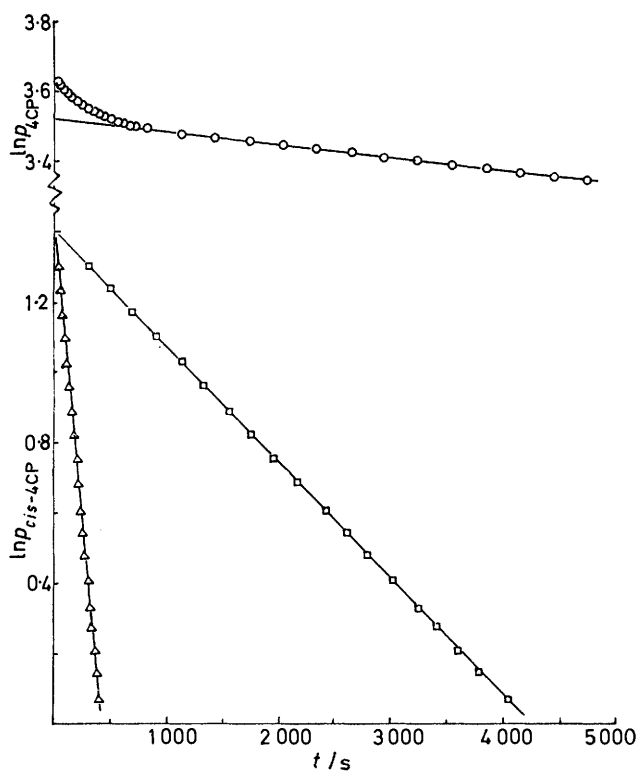


FIGURE 2 First-order plots for total reactant (○) (showing linear plot for *trans*-4CP after initial fast start), and for *cis*-4CP [obtained from equation (2)] (△, shown with a 10-fold time-scale expansion as □)

proof that the initial fast pressure change corresponds to decomposition of the *cis*-4CP.

**Kinetics of Reaction.**—Kinetic runs were carried out by RW at 564–640 K and 7–83 mmHg, and by RS at 520–

629 K and 20–85 mmHg. The pressure–time curves were interpreted by plotting  $\ln p_{4CP}$  against time, with  $p_{4CP}$  approximated by  $(2^a p_0 - p_t)$  where  $a$  is the dead-space factor;<sup>10</sup> this method of allowing for dead-space is elaborated and justified elsewhere.<sup>10b</sup> As noted by other workers,<sup>2</sup> such plots showed an initial fast reaction but were then linear for at least several half-lives of the decomposition (e.g. Figure 2, upper curve). The extrapolated intercept of the linear portion at  $t = 0$  always corresponded to the same fraction of the initial total pressure of 4CP ( $90 \pm 1\%$  in RS, where the initial pressure was obtained more accurately on account of the continuous automatic recording), and this fraction was the same within experimental error as the fraction of *trans*-isomer determined by n.m.r. spectroscopy. Coupled with the g.l.c. analysis showing near-complete depletion of the *cis*-isomer on the linear part of the curve, it is clear that, as postulated previously, the initial fast reaction is due to decomposition of *cis*-4CP and the remainder of the reaction is decomposition of the *trans*-4CP. Since the plots for the *trans*-decomposition were linear, and had slopes independent of the initial pressure, this reaction is first order and the slopes give the first-order rate constants  $k_{trans}$  in Table 1.

TABLE 1

Mean first-order rate constants  $k$  and population standard deviations  $\sigma$

T/K	No. of runs	$p$ /mmHg	<i>trans</i> -4CP		<i>cis</i> -4CP	
			$10^3 k_{trans}/s^{-1}$	$10^3 \sigma/s^{-1}$	$10^3 k_{cis}/s^{-1}$	$10^3 \sigma/s^{-1}$
Results of RW						
564.2	2	26, 29	4.46	0.12		
572.2	9	14–62	8.07	0.45	(5)	
595.2	10	12–43	44.8	2.2	(14)	
607.7	8	7–54	80.7	2.6	(30)	
619.2	8	21–83	187	15	(33)	
622.3	3	15–60	230	4		
627.0	3	26–30	340	4	(53)	
636.7	4	10–62	539	14		
640.2	2	27, 28	601	29		
Results of RS						
519.9	4	21–53	1.27	0.29	0.406	0.021
542.5	4	36–39	1.63	0.13	1.70	0.13
550.6	10	22–55	2.88	0.26	2.64	0.19
557.4	7	25–58	3.48	0.33	3.43	0.19
562.6	8	31–49	4.86	0.14	4.98	0.38
567.5	10	27–60	6.66	0.33	5.66	0.36
574.9	10	27–56	9.66	0.37	8.98	0.46
582.7	7	21–57	16.7	1.9	11.7	3.2
587.8	8	32–59	23.1	0.6	18.9	1.5
589.8	8	31–61	23.5	1.2	16.7	1.0
593.9	13	20–61	36.0	4.4	17.7	4.5
602.4	8	30–51	58.9	3.8	34.6	6.5
605.2	4	20–69	81.1	1.5		
629.2	5	21–85	311	14		

The kinetic behaviour of the *cis*-isomer can now be examined by subtracting the extrapolated pressure of *trans*-4CP from the total reactant pressure at times during the initial fast reaction [equation (2)]. Plots of  $\ln p_{cis}$  against time obtained by RS were linear for several half-lives

$$p_{cis} = p_{4CP} - p_{trans}^0 \exp(-k_{trans}t) \quad (2)$$

(e.g. Figure 2) and the slopes, which were independent of initial pressure, gave the first-order rate constants  $k_{cis}$  in Table 1. The manual pressure recording of RW precluded very accurate measurements of the *cis*-decomposition, but the rate constants obtained (Table 1) nevertheless show order-of-magnitude agreement with those of RS.

The temperature variations of  $k_{cis}$  and  $k_{trans}$  are illustrated in Figures 3 and 4. The data of RS for the *cis*-isomer give a normal Arrhenius plot (Figure 3), corresponding to the

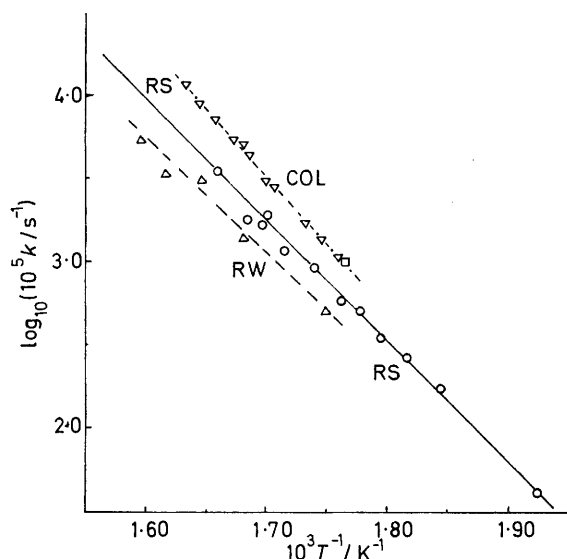


FIGURE 3 Arrhenius plots for decomposition of *cis*-4-chloropent-2-ene, showing results of RS (○), RW (△), Harding *et al.* (□), and COL (▽)

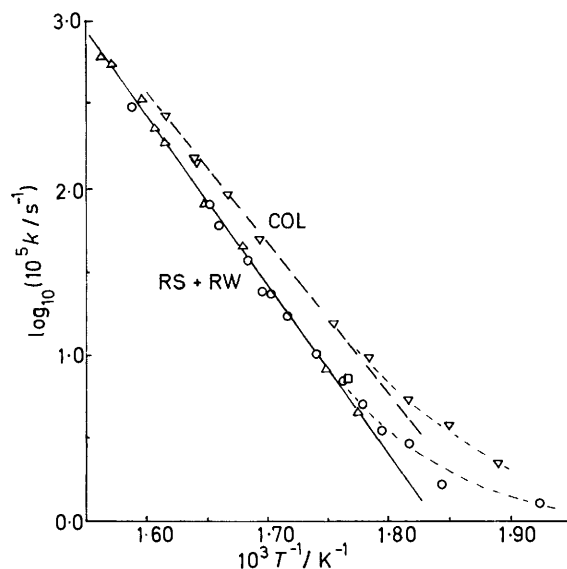


FIGURE 4 Arrhenius plots for decomposition of *trans*-4-chloropent-2-ene: symbols as in Figure 3

Arrhenius equation (3), in which equal weight has been given to each experimental point, and the error limits are

$$\log_{10}(k_{cis}/s^{-1}) = (9.85 \pm 0.46) - (131.3 \pm 5.1) \text{kJ mol}^{-1}/RT \ln 10 \quad (3)$$

95% confidence limits. For the *trans*-isomer (Figure 4), the higher temperature results of RS (at 575–629 K) are in excellent agreement with the data of RW (at 564–640 K). The Arrhenius parameters are indistinguishable [ $\log_{10}(A/s^{-1})$  (13.6 ± 0.4) and (13.8 ± 0.2) respectively, and  $E$  (194 ± 5) and (196 ± 2) kJ mol<sup>-1</sup> respectively], and the

Arrhenius equation for the combined results is (4). At temperatures below 575 K the *trans*-rate constants of RS

$$\log_{10}(k_{trans}/s^{-1}) = (13.86 \pm 0.26) - (196.8 \pm 3.5) \text{kJ mol}^{-1}/RT \ln 10 \quad (4)$$

show increasing deviations from the Arrhenius line of the higher temperature results, being nearly ten times higher than expected at 523 K. The reasons for this behaviour will be discussed later.

*Effect of Surfaces and Inhibitors.*—Runs were carried out in packed vessels, having surface : volume ratio 17 cm<sup>-1</sup> (RW) and 12 cm<sup>-1</sup> (RS) compared with 1.3 and 0.7 cm<sup>-1</sup> respectively for the unpacked vessels. After thorough seasoning of these vessels, as before, the rates of decomposition of both *cis*- and *trans*-4CP were the same within experimental error as those in the unpacked vessels, even at low temperatures where the Arrhenius plot for the *trans*-isomer is strongly curved (Table 2).

TABLE 2  
Effect of surface : volume ratio

$T/K$	Vessel	No. of runs	$p/\text{mmHg}$	$10^5 k_{trans}/s^{-1}$ (s.d.) <sup>a</sup>	$10^5 k_{cis}/s^{-1}$ (s.d.) <sup>a</sup>
529.3(RS)	{Packed	4	23–56	1.37(0.07)	0.80(0.09)
	{Unpacked <sup>b</sup>			1.2(0.3)	0.78(0.06)
545.1(RS)	{Packed	6	21–45	2.5(0.3)	1.7(0.2)
	{Unpacked <sup>b</sup>			2.4(0.2)	1.8(0.2)
573.1(RS)	{Packed	4	25–36	11.1(0.8)	8.7(0.6)
	{Unpacked <sup>b</sup>			10.0(0.4)	7.6(0.5)
593.2(RS)	{Packed	8	27–47	39(8)	17(5)
	{Unpacked <sup>b</sup>			33(4)	19(5)
595.2(RW)	{Packed	4	14–57	47(1)	
	{Unpacked <sup>b</sup>			10	11–43
636.7(RW)	{Packed	5	17–45	544(12)	
	{Unpacked <sup>b</sup>			4	10–62

<sup>a</sup> Population standard deviation of  $k$ . <sup>b</sup> Rate constants from Arrhenius plots (curve for *trans*-4CP); s. d. is a rough estimate for comparison only.

Runs in the presence of nitric oxide or *trans*-but-2-ene gave rate constants which were indistinguishable from those of uninhibited runs for *cis*-4CP and for *trans*-4CP in the temperature range of the linear Arrhenius plot (Table 3).

TABLE 3  
Effect of radical-chain inhibitors<sup>a</sup>

$T/K$	Inhibitor	No. of runs	$10^5 k_{trans}/s^{-1}$	$10^5 k_{cis}/s^{-1}$
523.3(RS)	{Butene	2 <sup>b</sup>	0.14	0.54
	{None		0.94 <sup>c</sup> (0.17) <sup>d</sup>	0.50
552.1(RS)	{Butene	4 <sup>e</sup>	2.16	2.48
	{None		3.41 <sup>c</sup> (1.83) <sup>d</sup>	2.69
574.9(RS)	{Butene	4 <sup>f</sup>	8.7	9.0
	{None		10	9.7
591.5(RS)	{Butene	5 <sup>g</sup>	33	23
	{None		30	19
627.0(RW)	{NO	3 <sup>h</sup>	337	
	{None		3	340

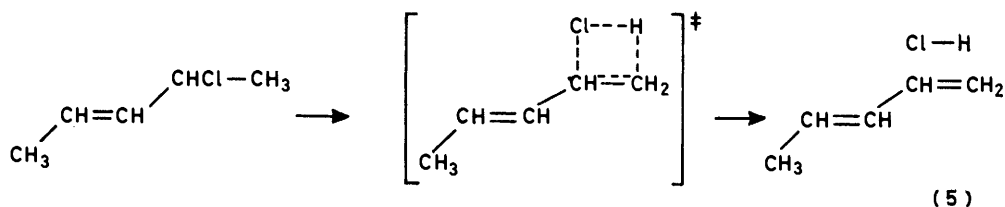
<sup>a</sup> Standard deviations for inhibited runs were similar to those for uninhibited runs. <sup>b</sup> Total initial pressure 45–54 mmHg; butene 31–49% of total pressure. <sup>c</sup> Interpolated on observed (curved) Arrhenius plot. <sup>d</sup> Calculated from (4) for linear Arrhenius plot extrapolated to lower temperatures. <sup>e</sup> 36–72 mmHg; 19–32% *trans*-but-2-ene. <sup>f</sup> 35–51 mmHg; 17–23% *trans*-but-2-ene. <sup>g</sup> 35–69 mmHg; 26–41% *trans*-but-2-ene. <sup>h</sup> 10–35 mmHg; 36–64% nitric oxide.

At temperatures < 575 K, butene had a marked retarding effect on the *trans*-decomposition, the implications of which will be discussed later.

## DISCUSSION

Thus the gas-phase thermal decompositions of *cis*- and *trans*-4-chloropent-2-ene in seasoned reaction vessels are clean first-order dehydrochlorination reactions (1) under all the conditions studied, and packing the reaction vessel had no significant effect on the reaction rates. Linear Arrhenius plots were obtained for *cis*-4CP over the whole temperature range studied (520—

The Arrhenius parameters for *trans*-4CP are very much in line with those for the four-centre decomposition of related compounds,<sup>12,13</sup> having a 'normal' *A* factor and an activation energy consistent with substitution by a vinylic group on the  $\alpha$ -carbon of an alkyl halide (compare, *e.g.*,  $E_a/kJ\ mol^{-1}$  for  $CH_3\cdot CH_2Cl$ , 245;  $CH_3\cdot CHCl\cdot CH\cdot CH_2$ , 203; *trans*-4CP, 197). The postulated mechanism is therefore as shown in (5).

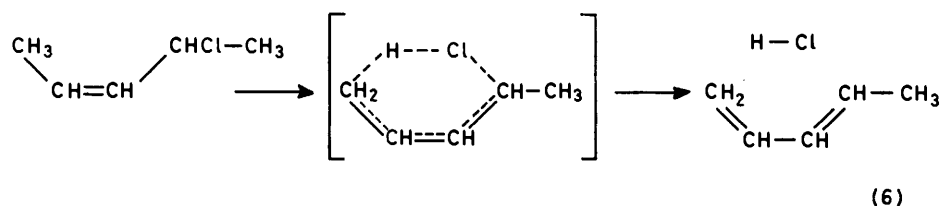


602 K) and for *trans*-4CP at 575—640 K, and at these temperatures neither reaction was affected by the addition of radical scavengers. It is concluded that the reactions under these conditions are homogeneous unimolecular processes.

The present results are compared with those of other workers in Figures 3 and 4. For *trans*-4CP (Figure 4), the rate-constants of RW, RS, and of Harding *et al.*,<sup>2</sup> are in good agreement, but those of Chytrý, Obereigner, and Lim (COL)<sup>5,6</sup> are substantially greater. For *cis*-4CP the measurement is more difficult, and neither RW nor Harding *et al.* claimed to obtain better than order-of-magnitude results; within this restriction they agree with RS. Again, however, COL obtain rate constants which are considerably higher than those of RS. In fact, COL reported rate constants corresponding to half-lives as low as 6 s for *cis*-4CP, and it seems very doubtful if these could have been measured with any accuracy in the type of apparatus used, which was

An alternative mechanism, which cannot be completely ruled out, involves a rate-determining isomerisation of *trans* to *cis*-4CP with a rate constant given by (4), followed by rapid decomposition of the *cis*-4CP. *cis*-*trans* isomerisations tend in fact to have lower *A* factors and higher activation energies than those in (4),<sup>12</sup> giving rate constants at 580 K of  $10^{-10}$ — $10^{-8}\ s^{-1}$  for olefins similar to 4CP, compared with  $10^{-4}\ s^{-1}$  for decomposition of *trans*-4CP itself. Although surface-catalysed isomerisation of *cis*-*trans*-4CP occurred readily in the cold gas-handling system, the packed-vessel (and inhibitor) work appears to rule out such effects in the reaction systems of RS and RW. It therefore seems unlikely that the isomerisation of *trans*-4CP can compete with four-centre decomposition, but experimental proof would be desirable.

The *A* factor and activation energy for *cis*-4CP are both much lower than for *trans*-4CP, and the *A* factor in particular suggests a six-centre mechanism (6), similar to



similar to that of RS. However, even at lower reaction rates, the results of COL are greater than those of RW and RS, and other factors must be operative. Since (a) the lower temperature results of RS indicate that free-radical reactions *can* occur in these systems (see below), (b) RW/RS explicitly demonstrated the absence of free-radical and surface effects in their system over most of the temperature range, whereas COL did not, and (c) the COL results are *higher* than ours, we therefore believe that the RW-RS results refer to simple unimolecular processes, while those of COL contain some free-radical and/or surface contribution.

<sup>12</sup> P. J. Robinson and K. A. Holbrook, 'Unimolecular Reactions,' Wiley, London, 1972; P. J. Robinson, 'Unimolecular Reactions,' in 'Reaction Kinetics,' ed. P. G. Ashmore, Specialist Periodical Report Vol. I, Chemical Society, London, 1975, p. 93.

that suggested previously for this and similar reactions.<sup>2,12,13</sup> The present *A* factor of  $10^{9.85}\ s^{-1}$  is lower than that found by these workers, but comparable with those reported for other types of six-centre reaction, *e.g.* of *gem*-diesters, allylic formates, and  $\beta$ -hydroxyolefins.<sup>12</sup>

For both reactions (5) and (6) the pentadiene produced is expected to be *trans*, and this is consistent with the observation of predominantly *trans*-PD, since the equilibrium proportion is *ca.* 70% *trans* at 520—640 K, and the isomers are to some extent interconvertible under the reaction conditions.

At temperatures below 575 K the Arrhenius plot for

<sup>13</sup> C. J. Harding, A. G. Loudon, A. Maccoll, P. G. Rodgers, R. A. Ross, S. K. Wong, J. Shapiro, B. S. Swinbourne, V. R. Stimson, and P. J. Thomas, *Chem. Comm.*, 1967, 1187.

*trans*-4CP curves upwards, as observed also by COL (Figure 4). The reaction under these conditions was still unaffected by surface:volume ratio (Table 2), ruling out a purely heterogeneous component of the reaction, but the addition of butene had a strong inhibiting effect, and in the limited studies which were made of this effect, the rate constants obtained in the presence of butene fell on the linear Arrhenius line extrapolated from the higher temperature results for the unimolecular process (5). It therefore seems likely that the upward curvature of the Arrhenius plot at low temperatures is due to a free-radical chain reaction which was maximally inhibited by the butene pressures used. The activation energy for this process is so low as to require heterogeneous initiation, and the absence of any effect of

surface:volume ratio on the rate suggests that both initiation and termination occur at the wall. Presumably the decomposition of the *cis*-compound is also subject to free-radical effects, but in this case the rate of the molecular decomposition is great enough to mask any such contribution, even at the lowest temperatures studied. It is curious that *trans*-but-2-ene should apparently be a more effective inhibitor than PD, and further studies are clearly needed to provide a better understanding of surface effects in these systems.

We thank the S.R.C. for awards to G. G. S. and M. J. W., and Dr. C. J. Harding for helpful discussions.

[7/1282 Received, 18th July, 1977]