

and [RH] stands for neopentane. The ratio R^0/R is the ratio of the relative yields of neopentanol in Table II.

The individual values of the relative rates k_5/k_2 obtained from eq 6 are given in the last row of Table II, and the average values are listed in Table III. In Table IV the relative rates from this work are compared with those found in other studies. In Table IV all the rates are expressed relative to that of CO_2 which provides a common basis.

The values obtained in this work agree well with those of other studies, determined in different systems and with $\text{O}(^1\text{D})$ from different sources. The values for N_2 and Xe , obtained from single experiments, are evidently in line with those from previous work,^{1,6,7} but the latter are based on more detailed determinations and are therefore more reliable quantitatively. SF_6 and He are found to be nonreactive as was observed before. The values for H_2 , CH_4 , and CO agree within a factor of 2 with those of Young, *et al.*¹⁷ This agreement is perhaps

as good as may be expected in view of the entirely different experimental techniques and the errors involved in both. The ratio $k_{\text{CH}_4}/k_{\text{H}_2} = 1.24$ estimated from the present results agrees well with the ratio of 1.15 found by De More.²⁴

On the other hand, there is a very large discrepancy of two orders of magnitude between the somewhat similar values for CO obtained in the present work and by Young, *et al.*,¹⁷ and that obtained by Clerc and Reiffsteck.²⁵ These values are 0.59, 0.28, and 55, respectively, and the difference is much larger than the experimental error in any of these studies. As already pointed out, both Young, *et al.*,¹⁷ and Clerc and Reiffsteck produced $\text{O}(^1\text{D})$ from O_2 by vacuum uv photolysis and flash photolysis, respectively, and both found $\text{O}(^1\text{D})$ to react with CO to form CO_2 , as opposed to deactivation to $\text{O}(^3\text{P})$ observed in the present work. The reasons for these discrepancies are not known.

(24) W. B. De More, *J. Phys. Chem.*, **73**, 391 (1969).

(25) M. Clerc and A. Reiffsteck, *J. Chem. Phys.*, **48**, 2799 (1968).

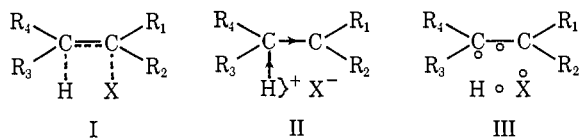
Gas-Phase Eliminations. XI.¹ The Pyrolysis of α -Chloro-*o*-xylene

A. G. Loudon, Allan Maccoll, and S. K. Wong

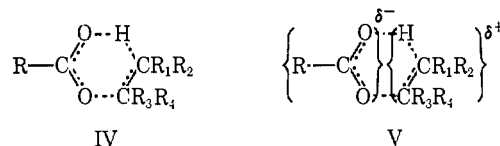
Contribution from the Williams Ramsay and Ralph Forster Laboratories, University College, London, W.C.1, England. Received May 19, 1969

Abstract: The kinetics of the pyrolysis of α -chloro-*o*-xylene to yield benzocyclobutene and hydrogen chloride in the temperature range 395–423° is reported. The reaction is first order, homogeneous, and unimolecular, the rate constants being expressed as $\log k_1 = 11.47 - (46,950/2.303RT)$ with k_1 in sec^{-1} . The facts are consistent with the decomposition occurring through a six-centered transition state.

The pyrolysis of alkyl halides has been extensively studied in many laboratories. Evidence has been presented for the polar character of the reaction.² On the basis of substituent effects, at or near the reaction center, the originally proposed homolytic four-centered transition state I has been replaced by the ion pair II or semi-ion pair transition state III.

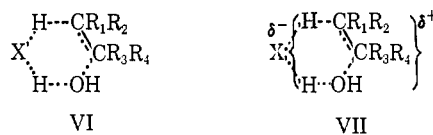


On the other hand, there is general agreement that the pyrolysis of esters proceeds through a six-centered transition state IV, as suggested by Hurd and Blunck.³ However, in this case too, a degree of polar character, as represented by the transition state V, has been suggested to explain the observed substituent effects.⁴ It



has also been suggested that Cope^{5a} and $\text{Claisen}^{\text{5b}}$ rearrangements proceed through a six-centered transition state.

The mechanism of the catalysis of the dehydration of alcohols by hydrogen halides has been investigated at length by Stimson and coworkers.⁶ The transition state in this case can be represented by VI or VII. A similar type of transition state was postulated by Ross and the



author,⁷ to explain the hydrogen bromide catalysis of the

(1) Part X: M. Dakubu, and A. Maccoll, *J. Chem. Soc., B*, 1248 (1969).

(2) A. Maccoll and P. J. Thomas, *Progr. Reaction Kinetics*, **4**, 136 (1967).

(3) C. D. Hurd and F. H. Blunck, *J. Amer. Chem. Soc.*, **60**, 2419 (1938).

(4) E. V. Emovon and A. Maccoll, *J. Chem. Soc.*, 227 (1964).

(5) (a) H. M. Frey and R. Walsh, *Chem. Rev.*, **69**, 103 (1969); (b) F. W. Schuler and G. W. Murphy, *J. Amer. Chem. Soc.*, **72**, 3155 (1950).

(6) J. T. D. Cross and V. R. Stimson, *Aust. J. Chem.*, **19**, 401 (1966).

(7) A. Maccoll and R. A. Ross, *J. Amer. Chem. Soc.*, **87**, 4997 (1965).

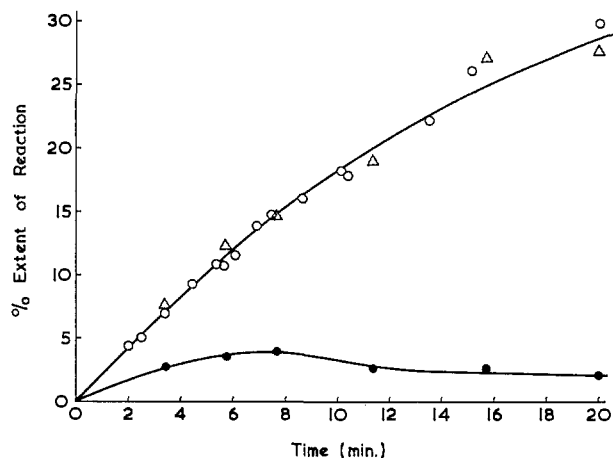
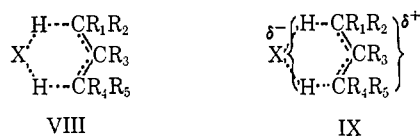
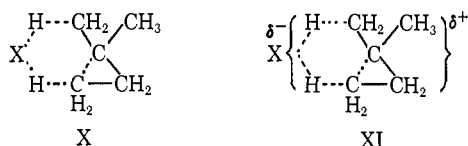


Figure 1. Equivalence of reactant disappearance and HCl appearance (415.6°): ○, HCl (by titration); △, chloride (by glpc); ●, benzocyclobutene (by glpc).

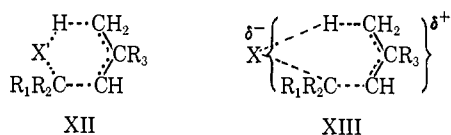
isomerization of the butenes (VIII or IX). Further, the



unique conversion of 1,1-dimethylcyclopropane into 2-methylbutene-1 as reported by Shapiro and Swinbourne⁸ confirms the six-centered transition state for this reaction (X, XI).



Rodgers⁹ studied the pyrolysis of α - and γ -methylallyl chlorides. In the case of the γ compound, the substance investigated was mainly the *trans* isomer. However, it was reported that fast starts occurred, which Harding¹⁰ has interpreted as being due to the decomposition of the *cis* compound. This worker has also studied the pyrolysis of α , α - and γ , γ -dimethylallyl chloride and has shown that the latter compound undergoes a particularly facile elimination. It was concluded that the transition state could be represented by XII or



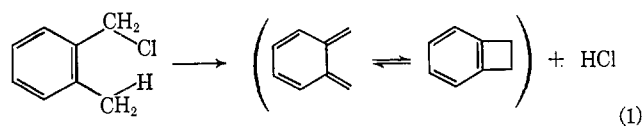
XIII. The present work describes the pyrolysis of α -chloro-*o*-xylene, which is also believed to proceed through a six-centered transition state.

The stoichiometry of the reaction was established (at least in the early stages) by pyrolyzing the compound in a flow system at 630° using nitrogen as a carrier gas. The yield of *o*-quinodimethane-benzocyclobutene (hereafter called benzocyclobutene) was 70% (see eq 1).

(8) J. S. Shapiro and E. S. Swinbourne, *Can. J. Chem.*, **46**, 1341 (1968).

(9) P. G. Rodgers, Ph.D. Thesis, University of London, 1966.

(10) C. J. Harding and A. Maccoll, *J. Chem. Soc.*, in press.



In a static system, consequent upon the initial elimination of hydrogen chloride, the benzocyclobutene may undergo four main reactions. They are (1) back-addition of HCl, (2) dimerization, (3) isomerization to styrene, and (4) abstraction of two hydrogen atoms to yield *o*-xylene. At a later stage still of the reaction, a number of minor products were observed including hydrogen, methane, ethylene, benzene, toluene, anthracene, and two unidentified compounds of molecular formulas $C_{15}H_{12}$ and $C_{15}H_{14}$. For these reasons the extent of reaction was determined (a) by analysis of the hydrogen chloride produced. Further, (b) the rate of disappearance of the substrate (determined by glpc with mesitylene as an internal standard) was measured. Benzocyclobutene (c) was also determined by glpc. The results are shown in Figure 1. Good agreement exists between (a) and (b), but the benzocyclobutene rises to a shallow maximum and then slowly falls. Confirmation of the stoichiometry (1) comes from overnight experiments. That the final pressure of hydrogen chloride is equal to the initial pressure of substrate is shown in Table I.

Table I. Stoichiometry of the Reaction

Temp, °C	p_0 , mm	p_{HCl} , mm
448	142.4	142.0
431	87.0	86.4
421	94.6	96.3
416	53.2	53.0

The disappearance of benzocyclobutene from the system was confirmed by introducing benzocyclobutene alone into the reaction vessel at 415°. After 2 min, a 20% reduction in pressure was observed, and a crystalline white solid was recovered from the products which was shown to be 1,2,5,6-dibenzocyclooctadiene. A glpc analysis of the liquid products showed styrene and *o*-xylene to be the major ones. At longer reaction times, all the products reported earlier from the long-term pyrolysis of α -chloro-*o*-xylene were observed. Thus it may be concluded that secondary reactions of benzocyclobutene are responsible for the complexity of the over-all reaction.

That the initial reaction was reversible was shown by carrying out the pyrolysis in the presence of added hydrogen chloride. The results are shown in Table II.

Table II. Reversibility of the Reaction

p_0 , mm	p_{HCl} (added), mm	% reaction ^a	Time, sec
136.4	0	27.6 (27.3)	380
157.8	64.0	20.8 (28.0)	390
75.9	58.4	18.3 (27.8)	390

^a The values in parentheses are those calculated from the runs to be described later.

It is readily seen that added hydrogen chloride represses the hydrogen chloride production. The reversibility of the reaction was verified by introducing benzocyclo-

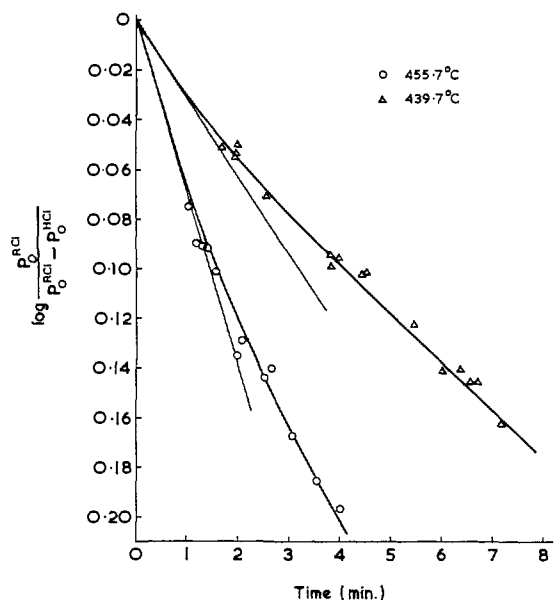


Figure 2. $\log p_0^{\text{RCl}}/(p_0^{\text{RCl}} - p_{\text{HCl}})$ vs. time.

butene and hydrogen chloride into the reaction vessel. Thus at 437°, with 75.3 mm of hydrogen chloride and 53.4 mm of benzocyclobutene, after 75 sec 7.8 mm of α -chloro-*o*-xylene was present in the products.

Rate coefficients were calculated from $k_1 = 2.303(t)^{-1} \log p_0/(p_0 - p_{\text{HCl}})$, where p_0 is the initial pressure of the substrate and p_{HCl} is the pressure of hydrogen chloride at time t . The curve of $\log p_0/(p_0 - p_{\text{HCl}})$ against time deviates from linearity after 10–15% reaction (Figure 2). However, the order could be established by studying the dependence of the per cent reaction on initial pressure. As Table III shows, the reaction is clearly of the first

Table III. Lack of Dependence of % Reaction on Initial Pressure

$T = 440^\circ$			$T = 423^\circ$		
p_0 , mm	Time, sec	% reaction	p_0 , mm	Time, sec	% reaction
64.0	110	11.2	48.2	150	7.3
87.8	115	11.8	69.0	148	7.2
151.2	117	11.6	145.3	153	7.8
203.0	119	10.6	285.2	150	7.0

order. To determine the first-order rate constants, the first-order rate coefficient was calculated, plotted against time, and extrapolated to zero time. Such a plot is shown in Figure 3. The results thus obtained over the temperature range 395–456° are recorded in Table IV. These were fitted to the Arrhenius equation $\log k_1 = 11.47 - (46,950/2.303RT)$, with k_1 in sec^{-1} . A good straight line resulted.

To check the homogeneity of the decomposition, runs were done in a packed vessel, in which the surface-to-volume ratio was increased by a factor of about 4.3 above that of the unpacked vessel. The maximum increase in rate constant was 8% (Table IV) verifying the essential homogeneity of the reaction. To test for the presence of radicals in the system, runs were carried out in the presence of propene and cyclohexene, substances known to be effective chain suppressors in halide pyrolysis. The results are shown in Figure 4. The

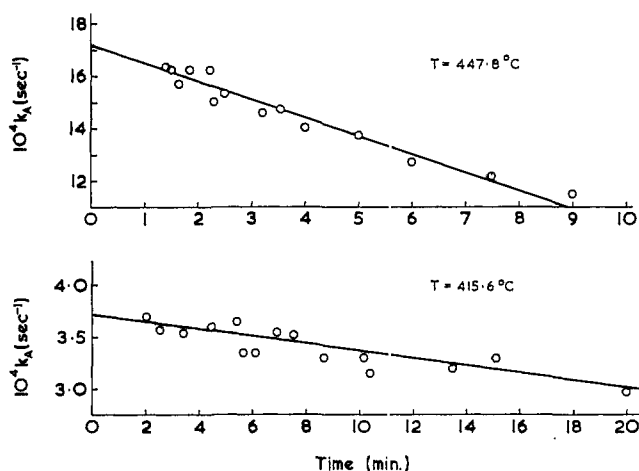


Figure 3. k_A (equal to $1/t \ln p_0^{\text{RCl}}/(p_0^{\text{RCl}} - p_{\text{HCl}})$) vs. time.

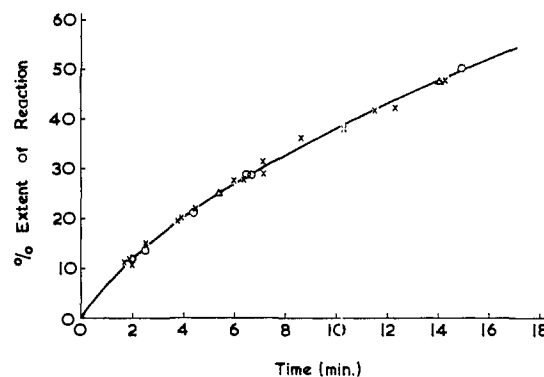
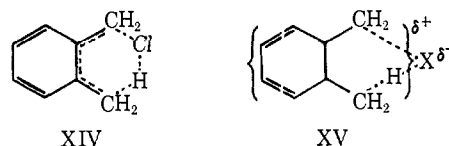


Figure 4. Effect of inhibitors (at 439.7°): X, absence of inhibitor; Δ, presence of propene; O, presence of cyclohexene.

per cent reaction is thus independent of the presence of inhibitors, and it may reasonably be concluded that the reaction does not proceed by a chain mechanism.

A preliminary survey of the α -chloro-*m*- and α -chloro-*p*-xylene showed that they decomposed at a rate appreciably slower than did the α -chloro-*o*-xylene. It would then appear that a specific *ortho* effect is being observed. Further, since the activation energy is lower than the carbon-chlorine bond dissociation energy, Benson gives 66 kcal mole⁻¹ for benzyl chloride;¹¹ a radical nonchain process can be ruled out. Thus it may be concluded that α -chloro-*o*-xylene decomposes by a unimolecular mechanism. This being so, it is difficult to envisage the decomposition taking place other than through a six-centered transition state, the extreme homolytic and heterolytic representations being XIV and XV. The question of the degree of polarity



of the transition state is at present under investigation. However, the low A factor observed ($10^{11.47} \text{ sec}^{-1}$), together with the low activation energy (46.95 kcal mole⁻¹) is consistent with the behavior of γ, γ -dimethylallyl chloride,¹⁰ for which a transition state of relatively low polarity has been postulated.

(11) S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960.

Table IV. Temperature Variation of the Rate Constants

Temp, °C	394.5	404.1 ^a	405.7	415.6	421.4 ^a	423.0
10 ⁴ k ₁ , sec ⁻¹	1.26	2.09 (2.06) ^b	2.30	3.75	5.35 (4.96)	5.35
Temp	431.4	439.7	440.5 ^a	447.8	455.7	
10 ⁴ k ₁ , sec ⁻¹	7.70	12.0	13.3 (12.4)	17.0	25.6	

^a Packed vessel. ^b The values in parentheses are calculated from the Arrhenius equation.

Experimental Section

A commercial sample (Eastman) of α -chloro-*o*-xylene was purified by vacuum distillation. The fraction with boiling point 120–121° (75 mm) was used. Identification of the compound was confirmed by mass spectral and nmr analysis. The glpc analysis of the sample showed the detectable impurities as being in total less than 0.2%. Benzocyclobutane was prepared by a modification of the method of Cava and Deana¹² and later in larger scale synthesized by pyrolysis of α -chloro-*o*-xylene in a flow system.¹³

The apparatus was essentially the same as previously described;¹⁴ the reaction vessels were seasoned with allyl bromide.¹⁴ The identification of products was done by mass spectral and glpc analysis. Because of the further reactions of the benzocyclobutane formed in the pyrolysis, the extent of reaction was not followed by pressure change but (a) determined by analysis of the hydrogen chloride produced and (b) by glpc analysis of the disappearance of the substrate. For case (a), in order to overcome the hydrolysis of the unreacted substrate in aqueous sodium hydroxide solution, the

(12) M. P. Cava and A. A. Deana, *J. Amer. Chem. Soc.*, **81**, 4266 (1959); J. A. Oliver and P. A. Ongley, *Chem. Ind. (London)*, 1024 (1965).

(13) S. K. Wong, Ph.D. Thesis, University of London, 1968.

(14) A. Maccoll, *J. Chem. Soc.*, 965 (1955).

reaction products were trapped in acetone at -197°. The hydrogen chloride was then estimated by titration with an ethanolic solution of sodium ethoxide using lacmoid as indicator. For case b a Perkin-Elmer F.11 chromatograph with flame ionization detector was used with mesitylene as an internal standard. The following calibration factors (*f*) defined by the equation (subscript c stands for compound; s, for standard)

$$\frac{(\text{pressure})_c}{(\text{pressure})_s} = \frac{(\text{moles})_c}{(\text{moles})_s} = f \frac{(\text{glpc area})_c}{(\text{glpc area})_s}$$

were determined and used: for α -chloro-*o*-xylene, 1.13; benzocyclobutene, 1.15; *o*-xylene, 1.10; styrene, 1.12.

Three columns were mostly used in this work, namely 4-ft 10% Apiezon L, 6-ft 8% Antarox CO-990, and 2.5-ft 10% Apiezon L in series with 2.5 ft of 8% Antarox CO-990.

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Pyrolysis of Ethylcyclobutane in the Gas Phase at High Pressures^{1a}

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Contribution from the Department of Chemistry, University of Rochester, Rochester, New York 14627. Received May 7, 1969

Abstract: The pyrolysis of ethylcyclobutane in nitrogen diluent gas was studied in the pressure range 100–2500 psi at 410°. In this pressure range, well into the high-pressure limiting region for this unimolecular reaction, the rate constant is given by $\log K = \log (4.54 \pm 0.03) \times 10^{-5} \text{ sec}^{-1} - (3.54 \pm 0.64) \times 10^{-5} (\text{psi})^{-1}P$, where *P* is the total pressure in pounds per square inch. From these results the volume of activation of the reaction is found to be $\Delta V^\ddagger = 28.2 \pm 5.3 \text{ ml/mole}$. This is in reasonably good agreement with a lower limit theoretical estimate of 21 ml/mole.

Cyclobutane and many of its derivatives undergo quite clean, well-characterized unimolecular decompositions in the gas phase; these have been studied intensively by Walters and his collaborators and by others,² and their pyrolyses by simple unimolecular mechanisms can be regarded as almost certainly established. These systems therefore provide an ideal testing ground for unimolecular rate theorists who wish to avoid interpreting data on reactions which are subsequently found to be heterogeneous or complex free-

(1) (a) This work was supported by a grant from the Air Force Office of Scientific Research; (b) send correspondence to this author at Department of Chemistry, Vanderbilt University, Nashville, Tenn. 37203.

(2) A. Maccoll and P. J. Thomas, *Progr. Reaction Kinetics*, **4**, 136 (1967).

radical processes. One of these systems is ethylcyclobutane, studied by Wellman and Walters³ over the pressure range 7–400 mm at 450° and over the range 10–200 mm over the temperature range 420–460°. The decomposition (to ethylene and 1-butene) is homogeneous and first order, and is not inhibited by propylene, toluene, or nitric oxide. The rate constant is given by $k = 3.6 \times 10^{15} / \exp(-62,000/RT) \text{ sec}^{-1}$. The rate constant was found to be independent of total pressure, indicating that the high-pressure limiting rate constant of the reaction has been reached; this is quite reasonable in view of the complexity of the molecule.

(3) R. E. Wellman and W. D. Walters, *J. Amer. Chem. Soc.*, **79**, 1542 (1957).