The results in Table I show that there is good agreement between the observed and the computed d-spacings for various reflections. The density of the crystals, as determined by specific gravity bottle using pure benzene as displacing liquid, was found to be 1.934 g./ml. at 25°, and the number of molecules of the dihydrate per unit cell was $4.05 \simeq 4$. From the systematic absence of the lines when l is odd in $00l$, the symmetry of the crystals corresponds to P_{222_1} (space group No. 17). The density of the crystals calculated from the X-ray data is 1.912 g./ml. Since the crystals are very hygroscopic, single crystal X-ray diffraction could not be carried out.

Acknowledgment.—The authors are thankful to Dr. Jagadish Shankar for helping in taking the powder pattern.

THE CHEMISTRY OF XYLYLENES. XIX. THE CO-PYROLYSIS OF *p*-XYLENE AND HEXACHLOROETHANE

BY L. A. ERREDE AND J. P. CASSIDY

Contribution No. 235 from the Central Research Laboratories of the Minnesota Mining and Manufacturing Company,[1] *St. Paul, Minn.*

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Dainton and Ivin[2] studied the thermal decomposition of hexachloroethane in a closed system. They found that the rate of reaction is appreciable even at 300°. The products were tetrachloroethylene and carbon tetrachloride. Chlorine was isolated, however, when the reaction was terminated before complete conversion. They concluded that the formation of tetrachloroethylene involved a chain reaction.

$$Cl\cdot + CCl_3CCl_3 \longrightarrow Cl_2 + CCl_3CCl_2\cdot \tag{1}$$

$$CCl_3CCl_2\cdot \longrightarrow CCl_2{=}CCl_2 + Cl\cdot \tag{2}$$

They suggested that the chain reaction was initiated either by thermal rupture of the C–Cl bond or the C–C bond

$$CCl_3CCl_3 \longrightarrow CCl_3CCl_2\cdot + Cl\cdot \tag{3}$$

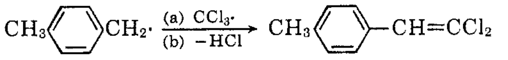
$$CCl_3CCl_3 \longrightarrow 2CCl_3\cdot \tag{4}$$

Calculation of bond dissociation energies based on molecular structure[3] gives 63 and 68 kcal. for the C–C and C–Cl bonds, respectively, in CCl_3CCl_3. This difference of 5 kcal. is quite significant and it suggests that C–C scission, not C–Cl, is the initiating process. The CCl_3 radicals thus produced abstract a chlorine atom from hexachloroethane, as shown in eq. 5, and thereby initiate the chain reaction exemplified by eq. 2 and 1.

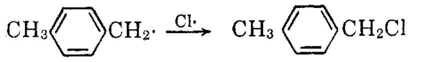
$$CCl_3\cdot + CCl_3CCl_3 \longrightarrow CCl_4 + CCl_3CCl_2\cdot \tag{5}$$

If C–C bond rupture is indeed the initiating reaction, then it should be possible to trap CCl_3 radicals in large amounts, whereas if C–Cl is the initiating reaction then it should be possible to trap the radical fragments CCl_3CCl_2 and Cl in about equal amounts.

In previous publications[4-6] it was reported that the primary radical fragments generated by fast flow pyrolysis of CCl_4 and of CCl_3H at low pressure could be trapped by quenching with a second stream of pyrolyzed p-xylene. When confluence occurred at the exit of the pyrolysis zone, p-methylbenzyl chloride and β,β-dichloro-p-methylstyrene were produced in equal amounts by random coupling of the primary radical fragments as indicated by equations 6 and 7.

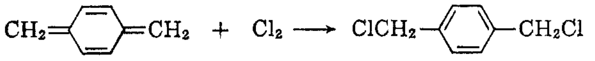


(6)

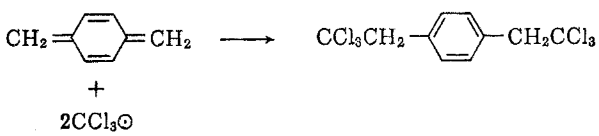


(7)

On the other hand, if confluence of the two fast flowing streams is delayed for only about 0.01 sec. after pyrolysis, the products are those produced by coupling of secondary radical fragments formed in the respective streams prior to mixing. Thus, coaxial pyrolysis of p-xylene and carbon tetrachloride gas streams, with confluence several inches beyond the furnace, gave α,α'-dichloro-p-xylene as a major product[5] (eq. 8), whereas the same experiment using p-xylene and chloroform gave α,α'-bis-trichloromethyl-p-xylene [also named p-bis-(β,β,β-trichloroethyl)-benzene] as a major product[6] (eq. 9).



(8)



(9)

To ensure isolation of the primary fragments in the present work, a gas mixture of p-xylene and hexachloroethane (mole ratio 3.5/1) was pyrolyzed and the products were isolated as described in the Experimental section.

The pyrolysis conditions used in this experiment were known to afford about 0.43 mole of p-methylbenzyl radicals.[7] Twenty-five per cent of these radicals were isolated as β,β-dichloro-p-methylstyrene, 3% as p-methylbenzyl chloride, <1% as α,α'-bis-trichloromethyl-p-xylylene, 47% as a mixture of 1,2-di-p-tolylethane and diphenylmethanes, and 24% as an ill defined non-distillable residue,[4,5] which probably formed as a result of decomposition of chlorocarbons during the separation by vacuum distillation. Carbon tetrachloride and tetrachloroethylene were also produced in some amount, but these were only identified qualitatively by mass spectrometric analysis.

The fact that the amount of β,β-dichloro-p-methylstyrene isolated was eight times greater than the amount of p-methylbenzyl chloride isolated demonstrates that C–C bond rupture of hexachloroethane to give CCl_3 radicals is the initiating reaction.

The isolation of about two grams of α,α'-bis-trichloromethyl-p-xylene indicated that the C–C bond

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[1] This work was done in the laboratories of the M. W. Kellogg Company. The data were acquired by the Minnesota Mining and Manufacturing Company with the purchase of the Chemical Manufacturing Division of the M. W. Kellogg Company in March, 1957.

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[5] Paper XVII: L. A. Errede and J. P. Cassidy, *ibid.*, **67**, 73 (1963).

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of hexachloroethane must continue to rupture at an appreciable rate, even in the post-pyrolysis zone, since it was demonstrated that *p*-xylylene does not accumulate to any appreciable amount until the pyrolyzate has cooled to about 700° at a point 5 inches away from the pyrolysis zone of the furnace.[5]

Experimental

The pyrolysis system shown in Fig. 1 of ref. 8 was modified to include a flask containing a weighed amount of hexachloroethane (419 g.) which was located between manometer 11 and the furnace 10. The temperature of this flask was kept at 95°. The pyrolysis system was evacuated to 5 mm. pressure and *p*-xylene (672 g.) was metered to the system at the rate of 0.035 mole/min. as described previously.[8] The gas stream passed through the flask containing warm hexachloroethane into the pyrolysis furnace where co-pyrolysis occurred at 1000° for an average residence time of 0.006 sec. The pyrolysate was collected in toluene (3.1) kept at −78°. At the end of the pyrolysis the resultant solution was warmed to room temperature and volatile components were removed by rapid evaporation at 100° and 60 mm. pressure. A sample of the distillate was analyzed by means of a mass spectrometer and the presence of tetrachloroethylene and carbon tetrachloride in small amounts was detected. The residue (95 g.) was stored at room temperature for several days. A small amount (2.1 g.) of needle-like crystals precipitated from the dark oil. These were removed by filtration and washed with hexane. The product was purified by vacuum sublimation at 100° and subsequent recrystallization from methanol to give pure white needles of α,α'-bis-trichloromethyl-*p*-xylene (also named *p*-bis-(β,β,β-trichloroethyl)-benzene; m.p. 174–175°) showing no depression with an authentic sample prepared and identified as described in a previous publication.[6] The infrared spectrum of this product was identical with that reported earlier.[6]

The oily mother liquor was dissolved in hexane and the resultant solution was chilled to −78° to precipitate any additional α,α'-bis-trichloromethyl-*p*-xylene or *p*-xylylene dichloride. No precipitate formed, however, and the hexane was separated by distillation at atmospheric pressure and the residue was separated further by distillation at 2.4 mm. to afford 5 major fractions: (1) 2 g., b.p. 70–90°, (2) 20.2 g., b.p. 96–97°, (3) 10.0 g., b.p. 120–135°, (4) 11.8 g., b.p. 135–150°, and (5) 15 g., residue. Fraction 1 was mostly *p*-methylbenzyl chloride and fraction 2 was almost pure β,β-dichloro-*p*-methylstyrene[4] as indicated by infrared analysis. Fraction 2 was recrystallized from methanol to yield 15 g. of β,β-dichloro-*p*-methylstyrene in the form of white platelets (m.p. 32.5–33.5°). The third and fourth fractions were identified by infrared analysis as mixtures of 1,2-di-*p*-tolylethane and alkylated diphenylmethanes. These were combined and dissolved in methanol. The solution was chilled to −78° and 1,2-di-*p*-tolylethane (6 g.) crystallized from solution in the form of pearl-white platelets (m.p. 74–76°).[9] Fraction 5 was a complex mixture of decomposition products containing phenyl and olefinic groups as indicated by infrared analysis and chlorine as indicated by a qualitative test for halogen.

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ON THE CALCULATION OF THERMAL TRANSPIRATION

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On the basis of the fundamental studies of a number of workers[1-6] Weber[7] developed his equation for the thermal transpiration of a gas along a closed cylindrical tube

$$\frac{dP}{dT} = \frac{P}{2T}\frac{1}{\alpha y^2 + \beta y + \mu}, \qquad y = d/\lambda \qquad (1)$$

where P is the pressure, T is the absolute temperature, d is the inside diameter of the tube, λ is the mean-free-path of the gas molecules, and the coefficients are given by the relations

$$\alpha \simeq \pi/128$$
$$\beta \simeq \pi/12$$
$$\mu = (1 + gy)/(1 + hy)$$
$$g - h + \beta = 1 \text{ or } {}^3/_4$$
$$g/h \simeq 1.25$$

Because thermal transpiration involves a transport phenomenon in a rarified gas, for which the usual methods of kinetic theory fail, the derivation of equation 1 contains a number of approximations. In particular a model is assumed in which the gas molecules are hard spheres of temperature dependent size, which undergo no specular reflection off the walls of the tube. Nevertheless, in view of the difficulty of determining pressures in the important submillimeter range, the existing body of thermal transpiration data should be considered with the same degree of reservation as the theory.

As pointed out by Weber, a useful approximate solution to equation 1 may be obtained by treating the left side as a quotient of finite differences. The solution may then be cast into one of several generalized forms in which a function of the temperature and pressure at the ends of the tube is obtained which is independent of the nature of the gas and the size of the tube. At present this approach is to be preferred not so much because the exact integration is tedious but because it permits data to be combined on a single, generalized plot. In this way it is indeed found difficult to reconcile sets of data from various sources with one another on the basis of any reasonable critique of the theory.

The solution suggested here is

$$\frac{dP}{dT}\frac{2T}{P} \simeq \frac{\Delta P}{\Delta T}\frac{2T}{P} \simeq \frac{1 - (P_1/P_2)}{1 - (T_1/T_2)^{1/2}} \equiv \Pi$$

$$\Pi = \frac{1}{\alpha y^2 + \beta y + \mu}, \quad T_2 > T_1 \qquad (2)$$

where y is some mean value between $y(P_1, T_1)$ and $y(P_2, T_2)$. This solution is exact in the limits where the theory is exact according to the relations

$$\lim_{y \to 0} (P_1/P_2) = (T_1/T_2)^{1/2}$$
$$\lim_{y \to \infty} (P_2 - P_1) = 0$$

The parameter y is calculated through the kinetic theory relation

$$\lambda P = kT/\pi(2)^{1/2}\sigma^2$$

where k is the Boltzmann constant and σ is the molecular hard sphere diameter. In the usual experimental arrangement P_2, T_2, and T_1, are known quantities and P_1 is to be calculated. The following convenient choice of y is made to avoid dependence on P_1

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