ing step. Since the chain length has been found to be long,[10] the groups at the ends of the chains can be neglected; likewise the heat contributed by reactions (1) and (3) is negligible compared to that of reaction (2).

If we further assume that the heat evolved in reaction (2) is independent of the chain length, then the percentage of heat evolution should be equal to the percentage of polymer formed. Consequently, the rates obtained by Norrish, *et al.*,[8,9] by measuring the percentage of polymer formation directly and those obtained in the present paper by measuring the percentage of heat evolved should be equal under the same experimental conditions.

In Fig. 2 we have shown the heat evolved in kcal./mole against the time of polymerization. Curves 1, 2, and 3 represent runs at 76.8° having catalyst concentrations of 1.0, 0.5, and 0.2%, respectively. The linearity of the initial slopes and their relationship to the square root of catalyst concentration is shown by graphing the thermal data against $t\sqrt{c}$, where c is the weight % of benzoyl peroxide (Figure 3). These observations are in agreement with the findings of Norrish and Brookman.[8] Quantitatively, our measurements obtained at the boiling point of benzene can be compared with theirs at 80°. Thus, using 0.20 weight % catalyst (0.0826 mole %), we obtained an initial slope, $\dfrac{d\left(\dfrac{\Delta Ht}{\Delta H_\infty} \times 100\right)}{dt} = 0.52.$ At 80° and with 0.0082 mole % of catalyst, Norrish and Brookman obtained an initial slope of 0.15%/min. Extrapolation to 0.0826 mole % catalyst, using the square root relationship, gives 0.48%/min.

The characteristic upward turn of the curves was attributed by Norrish and Smith[9] to an increase of bulk viscosity which reduces the chain-terminating reaction. The use of carbon tetrachloride as a solvent (Curve 4) delayed this upward turn as these authors have previously observed. A two-step reaction was shown by Curve 5, which was measured in methanol–water mixture. This was due to the fact that the mixture separated into two phases during the reaction and probably the reaction in each phase proceeded at a different rate.

Summary

1. A simple isothermal calorimeter is described which is suitable for determination of heats of polymerization. Its operation using methyl methacrylate is illustrated.

2. The heat of polymerization of methyl methacrylate was found to be 13.0 ± 0.2 kcal./mole. This value did not change with temperature or catalyst concentration within the limits investigated.

3. The rate of polymerization as measured by heat evolution agrees with measurements of other investigators using other experimental methods.

ROCHESTER, NEW YORK RECEIVED APRIL 7, 1945

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[10] Strain, *Ind. Eng. Chem.*, **30**, 345 (1938).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA, LOS ANGELES]

Cyclopropane Derivatives. I. Studies of the Photochemical and Thermal Chlorination of Cyclopropane

BY JOHN D. ROBERTS AND PHILIP H. DIRSTINE

Gustavson[1a] has reported that the photochemical chlorination of cyclopropane gave 1,1-dichlorocyclopropane and high-boiling compounds resulting from ring-opening reactions as the principal products. Small quantities of cyclopropyl chloride were isolated but the yields were unsatisfactory and attempts[1b] were made to prepare the monohalide by other methods. In beginning an investigation of the chemistry of cyclopropyl halides, we have studied the photochemical and thermal chlorination of cyclopropane in flow systems using conditions which were hoped to give useful yields of cyclopropyl chloride.

Experimental

The chlorination apparatus is shown in Fig. 1. U. S. P. cyclopropane (Ohio Chemical Company) was run from cylinder A through drying tube B (Anhydrone), gas-aspirator C and flowmeter D, mixed with chlorine (Dow) from cylinder E and flowmeter D′ and sent into the reactor G. The back pressure of the system was measured by the open tube manometer F. For the photochemical work, G was a 0.5 cm. i. d. × 250 cm. Pyrex tube shaped to form a grid about 6 cm. × 30 cm. Actinic energy was supplied by two No. 2 Photoflood bulbs at 7 cm. and a General Electric RS type sun-lamp at 8 cm. The grid was cooled by a strong air blast.

In the thermal runs G was a Pyrex tube (0.6 cm. i. d.) wound with Chromel A resistance wire and insulated with magnesite lagging. The tube was provided with several spaced take-offs so that the residence time could be varied without changing the flow rates. The take-offs were constructed of 1-mm. capillary tubing so that the transition time between reaction and quenching could be reduced to a negligible value. An exploring thermocouple was provided to measure the reaction temperature.

The hydrogen chloride in reaction products was removed by washing with water in tower H. The excess chlorine was absorbed in tower J with 5% sodium hydroxide solution. The gas stream was dried with calcium chloride (K) and Anhydrone (L). The cyclopropane was fractionated in column N and collected in Q. P and P′ were Dry Ice cooled condensers. The cyclopropane was refluxed rapidly in flask Q by means of an electric heater in

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[1] (a) Gustavson, *J. prakt. Chem.*, [2] **42**, 495 (1890); **43**, 396 (1891); (b) **46**, 157 (1892).

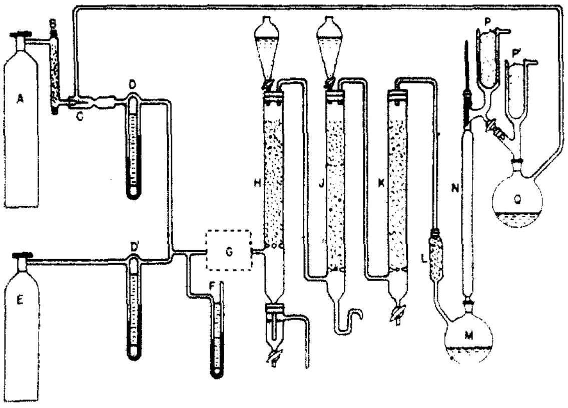

Fig. 1.

order to ensure that the gas being withdrawn from the vapor phase in this flask by the aspirator C was not contaminated with air drawn in through the top of the condenser P′. The aspirator which was constructed of glass tubing employed the stream of high pressure entering gas from tank A to create a suction to recycle the gas from flask Q. The gas-inlet was a small tube about the size of a fine hypodermic needle and terminated about 2–3 mm. in front of the throat, which was about 1 mm. in diameter. With these dimensions and working against the back pressure of the system about one and one-half to two volumes of gas were recycled for each volume of cyclopropane supplied from the cylinder. For a given tank of cyclopropane the running time could thus be considerably prolonged.

Table I

Reaction of Chlorine with Cyclopropane at Constant Flow (2.0 moles/hr. of C_3H_6 and 0.4 mole/hr. of Cl_2)

Average temp., °C.	Approx. residence time, sec.	% of total Cl_2 used	% of theoretical HCl formed	Approx. % of total Cl_2 in ring-opening reactions
215	0.2	2.5	2.5	0
300	.2	15.0	5.0?	10?
420	.1	85.0	70.0	15
480	.1	93.0 93.0	77.5 74.4	17
490	.1	95.2	81.5	14
215	.7	2.5	1.5	1.0
260	.7	2.5	1.5	1.0
330	.5	36.8	26.5	10
375	.5	79.0	60.0	19
475	.5	98.5	81.0	18
540	.5	99.9	85.0	15
550	.5	99.9	88.5	11

The chlorinated products were allowed to accumulate in flask M and were finally fractionated through an efficient column of the Whitmore–Lux[2] type. Fractionation of the products boiling higher than 1,1-dichlorocyclopropane was unsatisfactory. A complex mixture of dichlorohydrocarbons containing some dichloropropanes was obtained. The only substance which could be positively identified was 1,3-dichloropropane. Attempts to determine whether the *cis*- and *trans*-1,2-dichlorocyclopropanes are present in this mixture will be made in future investigations. The higher-chlorinated products were not investigated. The monochloro products were analyzed for unsaturation by the bromide–bromate method of Francis.[3] Physical properties of pure samples of cyclopropyl chloride and 1,1-dichlorocyclopropane were determined as follows: b. p. 43°, n^{20}_D 1.4101 and b. p. 74–75°, n^{20}_D 1.4400, respectively.

Experimental Results

Table I shows the extent of the thermal reaction of chlorine with cyclopropane (at constant flow) as a function of temperature and contact time. The difference between the total moles of chlorine used and the moles of hydrogen chloride produced may be taken as an approximate measure of the extent of ring-opening by halogen. Above 375°, the extent of ring-opening seems to fall off but this may be only apparent and due to an increase in the amount of dehydrohalogenation of the products.

The results of the analyses of the thermal reaction products are presented in Table II. No propene was ever detected on fractionation of the recovered cyclopropane. Therefore, thermal isomerization of the cyclopropane was unimportant with the brief residence times used in this work, despite the presence of hydrogen chloride. It is apparent, however, that the monochloride undergoes considerable thermal isomerization to allyl chloride and the extent of this process is determined by residence time and temperature.

The data for a typical photochemical run are tabulated in Table II. It is seen that hydrogen chloride was produced practically quantitatively on the basis of the chlorine consumption, showing that direct ring opening (resulting in the disappearance of chlorine with no corresponding liberation of hydrogen chloride) was not serious. The monochloro product was essentially free from allyl chloride and hence both the cyclopropyl free radical and cyclopropyl chloride were apparently stable with respect to isomerization

Table II

Products from the Photochemical and Thermal Chlorination of Cyclopropane

Method	Temp., °C.	Residence time, sec.	Moles, Cl_2/hr.	Moles C_3H_6/hr.	Mole C_3H_5Cl/hr.	% Allyl chloride in C_3H_5Cl	Mole $C_3H_4Cl_2$[a]/hr.	$\frac{C_3H_5Cl}{C_3H_4Cl_2{}^a}$	Moles HCl/hr.	Mole excess Cl_2/hr.	High boiling prod., /hr., g.
Thermal	500	0.1	0.41	2.4	0.16	1.5	0.0005	30	0.25	0.099	2.7
Thermal	500	.1	.67	4.0	.16	3.2	.0005	30	.28	.35	3.5
Thermal	510	.8	.67	4.3	.46	25.6	.003	15	.60	.001	4.8
Thermal	585	.05	1.7	3.0	.45	28.2	.003	15	1.09	.08	28.6[c]
Photo	<100	.9	0.91	5.8	.44	<0.2	.095	4.6	0.87	.047	6.5

[a] $C_3H_4Cl_2$ = 1,1-dichlorocyclopropane. [b] High-boiling product = residue after the distillation of the 1,1-dichlorocyclopropane. [c] Fractionation of this material gave 12.0 g. of an inseparable mixture of dichlorohydrocarbons, b. p. 53–78° (200 mm.), and 16.5 g. of 1,3-dichloropropane, b. p. 78–79° (200 mm.); n^{20}_D 1.4490.

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(2) Whitmore and Lux, This Journal, **54**, 3451 (1932).

(3) Francis, *Ind. Eng. Chem.*, **18**, 821 (1926).

under the reaction conditions. It is significant to note that much greater amounts of 1,1-dichlorocyclopropane are formed in the photochemical runs than in the thermal experiments. This may be due to inherent thermal instability of the dichloro compound itself or of the 1-chlorocyclopropyl free radical $(CH_2)_2\dot{C}Cl$ which is a probable intermediate in the formation of 1,1-dichlorocyclopropane. Studies of the thermal stability of the cyclopropyl halides should be of considerable aid in deciding this point.

Acknowledgment.—The authors are pleased to acknowledge the aid of Drs. W. G. Young and M. J. Schlatter to this investigation. One of us (P. H. D.) wishes to thank the Dow Chemical Company for a fellowship grant in support of this work.

Summary

1. The photochemical and thermal chlorinations of cyclopropane have been investigated as means for the practical preparation of cyclopropyl chloride.

2. Comparable yields of monohalide are obtained by both methods but the photochemical process is preferred because the product from the thermal reaction is contaminated with considerable amounts of allyl chloride.

LOS ANGELES 24, CALIFORNIA RECEIVED APRIL 23, 1945

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

The Photolysis of the Aliphatic Aldehydes. XII. Propionaldehyde

BY W. J. BLAEDEL AND F. E. BLACET

In the first paper of this series, quantum yields of propionaldehyde photodecomposition and polymerization were reported in considerable detail and a mechanism for the decomposition was proposed based upon limited quantitative data concerning the reaction products.[1] Since that time improvements have been made in analytical techniques which, when applied to acetaldehyde photolysis, have led to considerable change in our conception of aldehyde photochemical processes.[2] These analytical methods now have been applied also to the photolysis products of propionaldehyde.

TABLE I

COMBUSTION DATA SHOWING ETHANE TO BE THE ONLY HYDROCARBON PRODUCED IN PROPIONALDEHYDE PHOTOLYSIS

Experiment	Vol. sample, cu. mm.	Vol. sample + O_2	Vol. after combustion and P_2O_5	Vol. decrease (*a*)	Vol. after KOH	Vol. decrease (*b*)	Ratio *a*/*b*
1	26.47	198.43	141.53	56.90	96.83	44.70	1.27
	41.62	244.70	156.60	88.10	86.83	69.77	1.26
	27.04	231.69	176.06	55.63	131.79	44.27	1.26
2	24.62	183.67	126.22	57.45	80.85	45.37	1.26
3	47.04	261.21	155.36	105.85	72.03	83.33	1.27
4	50.06	271.09	162.49	108.60	76.87	85.62	1.27
	47.54	256.73	153.52	103.21	71.89	81.63	1.27
5	48.90	267.92	163.20	104.72	77.99	85.21	1.23
	48.65	266.32	160.46	105.86	74.43	86.03	1.23
6	35.13	219.92	140.09	79.83	76.89	63.20	1.26
7	33.73	247.75	173.96	73.79	113.14	60.82	1.22
	33.21	248.04	174.44	73.60	114.43	60.01	1.23
						Average ratio	1.253
						Ethane ratio	1.250

Experimental Results

The Non-condensable Products.—These were the products which remained in the gaseous phase at Dry Ice temperature. They consisted of hydrogen, carbon monoxide and ethane. No unsaturated hydrocarbons were found although numerous tests were made for them. Proof that the hydrocarbon was pure ethane is given in Table I. It made no difference what the conditions of irradiation were or which gas fraction pumped from the Dry Ice trap was taken for analysis; the ratio *a*/*b* obtained from combustion was always equal within experimental error to the theoretical ratio, 1.25, for pure ethane. Before combustion, carbon monoxide was removed by silver oxide and hydrogen by copper oxide and potassium hydroxide.

The number of moles of hydrogen and ethane per mole of carbon monoxide produced under a variety of experimental conditions are given in Table II. Each analytical result given is the average of from two to four determinations. The light source was an intense mercury arc used in conjunction with a crystal quartz monochromator.

Figure 1 shows graphically the extent of variation in hydrogen to carbon monoxide and ethane to carbon monoxide mole ratios found when pressure, intensity of radiation, temperature, and wave length in turn were made the variable, keeping the other three constant.

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[1] Leighton and Blacet, THIS JOURNAL, **54**, 3165 (1932).

[2] (a) Blacet and Volman, *ibid.*, **60**, 1243 (1938); (b) Blacet and Blaedel, *ibid.*, **62**, 3374 (1940).