other 4-g. portion of the ketene was added to the solution and the process repeated till 17.5 g. of the ketene had been used. Then the mixture was refluxed for a half hour, cooled and mixed with ice and dilute sulfuric acid. The ether layer was removed, washed with water, with 5% sodium carbonate solution and dried with calcium chloride. There was 15 g. of residue after removal of the ether. Most of it distilled at 97-100° (18 mm.) but there were higher (100-110°) and lower boiling fractions. The latter, which was collected at 65-70° (40 mm.) and which weighed about 1 g. possessed a mol. wt. of 147-156. The quantity at hand was insufficient for definite characterization.

The mol. wt. of the 97-100° (18 mm.) fraction was 162, 172 (calcd. for $C_8H_{16}O_3$, 172). This material was largely ethyl α-propionylbutyrate. In another similar run (from 5 g. of the ketene) the product was hydrolyzed by stirring with dilute alkali until dissolved and then acidified with 50% sulfuric acid. Ethyl propyl ketone was extracted from it with ether and characterized as the semicarbazone. The latter melted at 107-108° after two crystallizations from water. Michael[14] lists 111° as the m. p. for this semicarbazone.

Second Experiment.—Twenty-two grams (0.15 mole) of the redistilled ketene (b. p. 50-53° (11 mm.)) in 10- and 12-g. portions was treated as before with 0.16 mole of ethylmagnesium bromide. After the half-hour period of refluxing, the ether was distilled away and the temperature of the oil-bath progressively raised to 200°. A drop of paraffin lessened the tendency of the residue to foam. A distillate was obtained near 200°. The temperature was increased to 300° and finally a free flame was used. The 6 g. of liquid obtained was redistilled into two fractions: (1) 37-45°, 3 g.; (2) 45-110°, 2 g. The mol. wt. determination, high bromine content, and b. p. of fraction (1) confirmed its identity as ethyl bromide. Over half of fraction (2), on redistillation, boiled at 100-110°. The substance was unsaturated and 0.0034 mole of it (0.4265 g.) absorbed 0.0032 mole of bromine solution, indicative of one double bond. The mol. wt. values found were 113.7 and 117.4.

Ethylmagnesium Bromide and the Dimer of (A).—Fifteen grams of the dimer, diluted with 50 cc. of dry ether, was taken. Into it (ice cold) was dropped the calculated amount of ethylmagnesium bromide. The reaction mixture was worked up as with the ketene. These fractions were obtained at 12 mm.: 95-97°, 5 g.; 97-145°, 2 g.; 145-155°, 2 g.

The identity of the higher boiling fractions was not established but the 95-97° fraction was ethyl α-propionylbutyrate, the same as from the ketene itself. Hydrolysis yielded ethyl propyl ketone as before; semicarbazone, m. p. 108.5-109°.

Summary

Ethyl ethylketenecarboxylate was prepared by direct dehydration of ethyl hydrogen ethylmalonate with phosphorus pentoxide. The behavior was studied of this ketene and its dimer toward phenyl- and ethylmagnesium bromides. Addition was found to occur preferentially at the ketene carbonyl, giving β-keto esters. No allene type was produced when the addition product of the ketene and ethylmagnesium bromide was pyrolyzed. Instead, ethyl bromide and an unsaturated compound were formed.

Ethyl malonate was converted to ethyl ethylmalonate by the use of ethyl sulfate and sodium ethoxide.

EVANSTON, ILLINOIS RECEIVED JUNE 24, 1935

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[14] Michael, THIS JOURNAL, **41**, 393 (1919).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Reaction between Ethylene and Chlorine in the Presence of Chlorine Acceptors. The Photochlorination of Ethylene

BY T. D. STEWART AND BERNHARDT WEIDENBAUM

This work was instigated by the concept of the reaction between ethylene and chlorine being a chain reaction, similar to the photochemical formation of benzene hexachloride from benzene and chlorine, which has been shown to have a quantum efficiency of the order of 100. That these two reactions have a common intermediate was shown by Stewart and Hanson[1] when they found that ethylene passed into a solution of chlorine in benzene in the dark yielded benzene hexachloride, in the ratio of about ten moles of chlorine reacting with benzene for each one reacting with ethylene, or an induction factor of ten.[2]

These photochlorinations are now commonly considered to involve chlorine atoms or possibly the complex Cl_3, with no clear way as yet of distinguishing their relative importance.[3] The chlorinations of hydrogen and of saturated hydrocarbons involve the same variables.

The Photochlorination of Gaseous Ethylene.—To ascertain that this addition reaction, normally

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[1] Stewart and Hanson, THIS JOURNAL, **53**, 1121 (1931).

[2] Two years ago, Mr. Harold Pitt, in this Laboratory, succeeded occasionally in obtaining an induction factor of 70-100. Rigid exclusion of oxygen and low partial pressures of ethylene permitted the longer benzene-chlorine chains.

[3] Dickinson and Carrico, THIS JOURNAL, **56**, 1478 (1934).

slow in the gas phase, proceeds without complication as a photochemical reaction, a mixture of chlorine and ethylene gases, each at a pressure of ten centimeters of sulfuric acid, was illuminated by light of approximately 4360 Å.

Preparation of Materials.—Chlorine was prepared by heating a tube of copper chloride which was sealed in the line. Ethylene was prepared from the dibromide with zinc, scrubbed with 95% alcohol, dried over calcium chloride and phosphorus pentoxide and condensed in liquid air. The first portion upon evaporation was discarded, the rest stored under pressure in a bulb sealed to the line. There was rigid exclusion of water and oxygen in the line. Electrolytic hydrogen passed over hot copper and through a liquid air trap was used.

The light source was a 500-watt tungsten lamp, about 46 cm. from the 130-cc. reaction flask. Two Zeiss monochromator filters were used; calibrated screens varied the light intensity. Evacuation was achieved with a mercury diffusion pump. The partial pressure of each gas was measured on a sulfuric acid manometer, which also served to follow the reaction rate.

In every experiment the reaction flask was first "cleaned up" by exploding a mixture of hydrogen and chlorine in it, and then evacuating to a pressure less than 10^{-5} mm. of mercury. The criterion of cleanliness was the absence of appreciable induction period upon explosion.

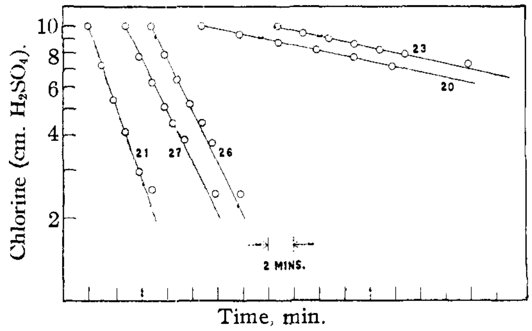

Fig. 1.—The photochemical addition of chlorine and ethylene gases.

If the pressure of chlorine is plotted against time on semi-logarithmic paper, a linear relationship is found to exist during the early part of the reaction. As the reaction proceeds, deviation from linearity is observed; this is caused probably by a concurrent reaction, such as the chlorination of the addition product. In Fig. 1 the results of a few experiments, in which the initial pressure of the reactants is kept constant and the light intensity varied, are plotted. Table I gives a summary of the initial rates as a function of the intensity of the incident light; the rates are given in arbitrary units and were obtained from the slopes of the curves.

TABLE I

EFFECT OF LIGHT INTENSITY UPON THE RATE OF ADDITION OF ETHYLENE AND CHLORINE

Experiment number	Light intensity	Rate
2-21	1	3.39
2-26	0.67	2.31
2-27	.67	2.31
2-28	.47	1.63
2-29	.47	1.62
2-18	.379	1.24
2-22	.372	1.23
2-19	.148	0.54
2-24	.148	.54
2-20	.059	.25
2-23	.059	.25

These data are plotted in Fig. 2, from which it is apparent that a linear relationship exists between the incident light intensity and the initial rate of the reaction. The rate law may then be expressed

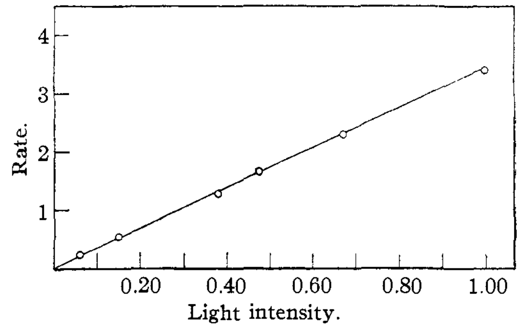

Fig. 2.—Effect of light intensity.

$$\frac{-d(Cl_2)}{dt} = kI_{abs.} = KI_0(Cl)_2$$

Although the quantum yield was not measured, there is little doubt that it is very large, since explosions of these gases are obtained when illuminated under the proper conditions.

It is possible to derive this rate law on the basis of several mechanisms, in each of which one chain-continuing intermediate (Cl or Cl_3) reacts much more rapidly with ethylene than in any other way, to form another intermediate which may either continue the chain or terminate the chain at the walls. For instance

$$Cl_2 + h\nu \longrightarrow Cl + Cl \qquad (1)$$
$$Cl + Cl_2 \longrightarrow Cl_3 \qquad (2)$$
$$Cl_3 + C_2H_4 \longrightarrow C_2H_4Cl_3 \qquad (3)$$

$$C_2H_4Cl_3 \longrightarrow C_2H_4Cl_2 + Cl \qquad (4)$$
$$C_2H_4Cl_3 + W \longrightarrow C_2H_4Cl_2 + {}^1/_2Cl_2 \qquad (5)$$

or

$$Cl_2 + h\nu \longrightarrow Cl + Cl \qquad (1)$$
$$Cl + C_2H_4 \longrightarrow C_2H_4Cl \qquad (2)$$
$$C_2H_4Cl + Cl_2 \longrightarrow C_2H_4Cl_3 \qquad (3)$$
$$C_2H_4Cl_3 \longrightarrow C_2H_4Cl_2 + Cl \qquad (4)$$
$$C_2H_4Cl_3 + W \longrightarrow C_2H_4Cl_2 + {}^1/_2Cl_2 \qquad (5)$$

The rate determining step in each case is equation (4), and either mechanism yields the experimental rate law. In any case it is evident that ethylene must have a very high collision efficiency with the intermediate, in order that within wide limits its concentration should not affect the rate.[4]

The Reaction of Chlorine in a Mixture of Ethylene and Hydrogen.—This reaction was measured in the apparatus just described. Before each experiment the walls were "cleaned up" as usual. The reaction with ethylene could be followed by the manometer at room temperature; that with the hydrogen was measured by taking a manometer reading with the vessel in a liquid air-bath whose temperature was measured with a gold resistance thermometer.

Table II gives some of the data obtained. Some experiments of identical results are omitted, as well as measurements taken at intermediate time intervals. The table headings are self-explanatory, except that the manometer reading is arbitrary and differences only are significant. The initial partial pressures are measured; final ones are calculated from the manometer readings on the assumption of a simple addition reaction to ethylene, and in experiments 2–9 and 2–11, from measured loss of hydrogen.

In the dark reaction no detectable reaction with hydrogen occurred during the ethylene–chlorine reaction. Even in the presence of light, a hydrogen–ethylene ratio of 9.64/1 permitted only 10.7% of the total chlorine reacting to react with the hydrogen, or a reactivity in favor of the ethylene of about 81-fold. If this be interpreted solely in terms of the difference in the heats of activation of the two reactions, since the heat of activation of the photochemical hydrogen-chlorine reaction is 6000 calories, that for the ethylene–chlorine photochemical reaction is less than 1400 calories.

TABLE II

THE REACTION IN MIXTURES OF ETHYLENE, CHLORINE AND HYDROGEN

Expt.	Partial pressures, cm. Chlorine	Hydrogen	Ethylene	Manometer reading	Time, min.	Temp., °K.
	Part A. Dark reaction					
2–1	47.48	27.95	16.40	102.5	0	298
	...	...	...	18.95	0	83.79
	45.78	27.95	14.70	100.8	15	298
	...	...	...	18.95	15	83.88
	ca. 31.0	*ca.* 27.0	0	86.0	α[a]	298
	...	...	...	18.65	α[a]	83.91
2–2	32.95	19.35	11.70	73.2	0	298
	...	...	...	16.0	0	83.61
	21.25	19.35	0	61.5	1080	298
	...	...	...	16.0	1080	83.81
	Part B. Illuminated by 500-watt lamp					
2–5	26.9	20.1	17.9	75.1	0	294.5
	...	...	...	6.45	0	83.81
	14.2	20.1	15.2	62.4	45	294.5
	...	...	...	6.45	45	83.90
2–9	10.0	92.5	9.6	125.5	0	294.0
	...	...	...	38.3	0	82.73
	1.66	91.61	2.15	118.05	50	294.0
	...	...	...	38.05	50	82.73
2–11	11.4	92.55	0	115.9	0	294.0
	...	...	...	38.65	0	83.63
	0	81.15	...	115.9	50	294.0
	...	...	...	35.40	50	83.81

[a] To complete the reaction the 500-watt lamp was held close to the reaction vessel until perceptible change in the manometer ceased. The total pressure drop, 16.5 cm., was practically equal to the original ethylene pressure.

The Ethylene–Chlorine Reaction in Ethylene Chloride and in Pentane as Solvents.—Commercial ethylene chloride was refluxed over both calcium chloride and phosphorus pentoxide for several hours each, and distilled into dried bottles at 83.4–83.6°. The purifications of the *n*-pentane,[5] ethylene and chlorine have been described.[6] Carbon tetrachloride was refluxed for twelve hours with chlorine and iodine, washed with alkali, acid and water successively, dried with calcium chloride and refluxed over phosphorus pentoxide for six hours. It was distilled at 76.6° into carefully dried bottles.

Procedure.—Stock solutions of the olefin and chlorine in the solvents concerned were kept at 0° in an ice-bath. The reaction vessel, which usually was a 125-cc. glass-stoppered Erlenmeyer flask, was also immersed in an ice-bath. A known amount of each solution was pipetted into

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[4] It is estimated that if chlorine and ethylene, each at a pressure of 0.001 of an atmosphere, were illuminated in a 130-cc. cylindrical reaction vessel, the rate of disappearance of chlorine atoms by reaction with ethylene should be nearly equal to the rate at which they combine at the wall.

[5] The refractive index of the carefully purified pentane was measured in a Pulfrich refractometer, referred to air at 20°.

n^{20}_D 1.35750 n^{20}_α 1.35572
n^{20}_β 1.36187 n^{15}_α 1.35854

[6] Stewart and Weidenbaum, THIS JOURNAL, **57**, 1702 (1935).

the reaction flask; as a rule the olefin was added first and then the chlorine. After the reaction had proceeded for the time interval desired, it was "quenched" by adding an aqueous solution of potassium iodide. The iodine liberated was determined by titration with sodium thiosulfate of suitable strength, using the method suggested by Liebhafsky.[7] The amount of hydrogen chloride produced, which was a measure of the induced substitution reaction, was obtained then by titrating the contents of the reaction flask with sodium hydroxide of suitable strength; brom cresol green was used as the indicator for this titration because of the distinctness of the end-point in spite of the two phases being present.

The stock solution of olefin was analyzed by adding a known amount of a solution of bromine in carbon tetrachloride, which was approximately twice the amount that would be required by the sample of olefin used. The mixture was kept in the dark for two hours at 0°. At the end of this time the uncombined bromine was determined by adding an aqueous solution of potassium iodide and titrating with sodium thiosulfate.

Experimental Results.—A large number of experiments using ethylene dichloride as the solvent for the reaction between chlorine and ethylene were performed with various changes in the experimental conditions. These included various ratios of the concentration of chlorine to that of ethylene over a range of 0.5 to 2, different treatment of the reaction vessel, such as burning it out in order to clean up the walls, variation of the temperature from 0 to 25°, and changes in the order of mixing the reactants.

When the concentration of each reactant was 0.05 *M* or larger, the reaction proceeded too rapidly to allow a study of its kinetics to be made. The induction factor was never greater than 0.1; here the induction factor is given by the ratio of the number of moles of hydrogen chloride produced to the number of moles of chlorine that are used by the olefin in the addition reaction.

Pentane was next used as the solvent. Here again the reaction was exceedingly rapid, being over 95% complete in fifteen seconds, but an induction factor as large as 2.8 was observed. Some typical results are given in Table III.

The members of the last two pairs of experiments differed only in the order in which the reagents were added.

TABLE III

THE CHLORINATION OF PENTANE INDUCED BY ETHYLENE

Time, seconds	Concentration × 10^3 Chlorine	Ethylene	Induction factor
30	8.6	25.0	2.8
30	16.0	6.7	0.85
30	3.8	13.0	2.3
30	3.5	18.7	2.6
60	1.33	1.85	1.5
60	3.64	0.93	0.7
60	3.64	0.93	0.6
60	0.57	1.85	1.9
60	0.57	1.85	1.9

It is seen that from 35.5 to 73.6% of the reacting chlorine produces hydrogen chloride. Moreover, if at a given initial chlorine concentration the initial ethylene concentration is increased, more substitution occurs (items 3, 4, 6 and 7); conversely a relative increase in the chlorine concentration decreases substitution (items 5 and 8). The substitution is probably upon the pentane, as the use of ethylene dichloride as a solvent for the same reactants produced but about 10% substitution at a maximum; pentane and chlorine alone do not react in the time allowed.

The question arises as to whether the intermediate in this induced substitution of pentane is the same molecule as the intermediate in its photochemical chlorination. Chlorine atom may be an intermediate in both the chain reaction of addition to ethylene and the chain reaction of substitution upon pentane, but as in the case of the hydrogen–chlorine reaction, ethylene should be an efficient inhibitor for the pentane–chlorine reaction. Increasing ethylene should decrease, not increase, the substitution if chlorine atoms were responsible. It would appear then, that some derivative of ethylene is the intermediate in the substitution reaction. If chlorine atom were competed for by both ethylene and chlorine, and if of the two products C_2H_4Cl promoted substitution and Cl_3 promoted addition, the facts could be qualitatively accounted for. We may then write

(1a) $Cl + Cl_2 \longrightarrow Cl_3$
(1b) $Cl + C_2H_4 \longrightarrow C_2H_4Cl$
(2) $C_2H_4 + Cl_3 \longrightarrow C_2H_4Cl_3 \longrightarrow C_2H_4Cl_2 + Cl \ldots$
(3a) $C_2H_4Cl + Cl_2 \longrightarrow C_2H_4Cl_3 \longrightarrow C_2H_4Cl_2 + Cl \ldots$
(3b) $C_2H_4Cl + C_5H_{12} \longrightarrow C_2H_4 + C_5H_{11} + HCl$
(4) $C_5H_{11} + Cl_2 \longrightarrow C_5H_{11}Cl + Cl \ldots$

with appropriate chain breaking steps. While the data do not permit a quantitative test of this mechanism, it may be interesting to derive an

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[7] Liebhafsky, THIS JOURNAL, **53**, 165 (1931).

expression based upon it, for the instantaneous values of the induction factor as functions of the relative concentrations of reagents and of the various specific reaction rate constants. Assuming that the source of chlorine atoms is thermal decomposition and that any possible substitution due to the reaction

$$Cl + C_5H_{12} \longrightarrow C_5H_{11} + HCl$$

is slow compared to reaction (3b) above, and assuming as a chain terminating reaction

$$C_2H_4Cl_3 + W \longrightarrow C_2H_4Cl_2 + {}^1/_2Cl_2$$

we may write

$$\text{Induction factor} = \frac{d(HCl)}{dt} \Big/ \frac{d(C_2H_4Cl_2)}{dt} = K_{1b}K_{3b} \times \frac{(C_2H_4)}{(Cl_2)} \times \frac{(C_5H_{12})}{K_{1a}K_{3b}(C_5H_{12}) + K_{1a}K_{3a}(Cl_2) + K_{1b}K_{3a}(C_2H_4)}$$

The subscripts relate the specific reaction rate constants to the equations above. It is seen that should by accident the competitive reactions 1a, 1b and 3a, 3b, be equal in rate, so that $K_{1a} = K_{1b}$ and $K_{3a} = K_{3b}$, the expression reduces to

$$\text{I. F.} = (C_2H_4)/(Cl_2)$$

since here (C_5H_{12}) is large compared to (C_2H_4) or (Cl_2) Similarly, if ethylene be in large excess, or excessively reactive, causing only equations (3a) and (3b) to operate as competitive, it reduces to

$$\text{I. F.} = K_{3b}(C_5H_{12})/K_{3a}(Cl_2)$$

It should be stressed that the induction factors measured are integrated values over wide ranges of relative concentrations of reagents.

A very rapidly reacting ethylene should produce more substitution (reaction 1b being favored) than a slowly reacting one. The compound to be substituted must be very reactive, favoring reaction 3b over reaction 3a; ethylene chloride as solvent is perhaps for this reason less attacked than pentane. It is thus seen that ethylene does inhibit the normal chain of pentane chlorination; if it did not, conditions would be found where the induction factor approximated the quantum efficiency factor in the photochemical reaction. Experience with the induced benzene–chlorine addition lends credence to this expectation. But in addition to this inhibition, a new path is furnished for the substitution reaction, favored by excess of ethylene. Further evidence of this interpretation will be presented in a succeeding paper.[8]

Summary

1. The photochlorination of gaseous ethylene proceeds at a rate proportional to the chlorine concentration at constant light intensity, and independent of the ethylene concentration.

2. Practically no hydrogen reacts in a mixture of hydrogen, chlorine and ethylene, either in the dark or when illuminated, while the ethylene–chlorine reaction goes to completion.

3. The ethylene–chlorine reaction in ethylene dichloride solution is very rapid, and involves less than 10% of the chlorine in substitution; while in pentane solution from 37 to 73% of the chlorine substitutes, and the amount of the substitution is increased by an increase in the ethylene/chlorine ratio.

BERKELEY, CALIF. RECEIVED JULY 22, 1935

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[8] Stewart and Smith, THIS JOURNAL, **52**, 2869 (1930), found that excess chlorine, when reacting with ethylene on surfaces coated with the reaction products, served to decrease the reaction rate and *increase* substitution. They obtained a maximum induction factor of unity, much higher than is found here in homogeneous solution. The difference in behavior is very real; one possible reconciliation is as follows. The series of reactions given above still holds, but the intermediate $C_2H_4Cl_3$ may react at the wall, not alone to produce Cl_2 as is often assumed for a chain breaking step, but also to give hydrogen chloride and products which no longer propagate a chain. Thus excess chlorine, winning in the competition for chlorine atom, might give an intermediate with ethylene which decomposed homogeneously one way, but at a surface differently. This could be true particularly on a surface which did not catalyze the chlorine–ethylene addition, since such a surface might also not catalyze recombination of chlorine atoms and thereby would give opportunity for the type of decomposition leading to substitution.