

is 62 min., no enolization occurs under these conditions except that incidental to the decarboxylation.

Kinetic Procedure.—The apparatus used to follow the rate of decarboxylation of β -keto acids consisted of a 20-ml. glass-stoppered flask connected with small diameter Tygon tubing to an inverted 5- or 10-ml. buret. The buret was inverted over water saturated with carbon dioxide. The flask and stopper were kept completely submerged in a Nujol thermostat constant to $\pm 0.05^\circ$.

The solvent (15 ml.) was introduced into the flask, saturated with carbon dioxide, and placed in the thermostat. The acid to be decarboxylated was introduced into the flask and the flask shaken until the acid dissolved. The initial concentration of acid was as near 0.02 *M* as possible. With *m*-nitrobenzoylacetic acid the limit of solubility appeared to be about 0.01 *M*. For each point, the flask was shaken for 30 seconds, and then 30 seconds later the buret

reading and time were recorded. The first point was used as zero time.

First-order rate constants were calculated from the half-life ($k_1 = 0.693/t_{1/2}$), obtained by plotting fraction unreacted against time on semilogarithmic paper and fitting the best line to the data by eye. In general the plots were straight lines out to 95% reaction.^{3,8}

Since dimethylacetoacetic acid could not be isolated, a slightly different procedure was followed in this case. The solvent was introduced along with an appropriate amount of barium dimethylacetoacetate and the mixture allowed to reach thermostat temperature. Less than one equivalent of sulfuric or phosphoric acid-*d*₄ was added, and the same procedure followed as above.

The rate constants reported in Table I are usually averages of from two to six kinetic runs. The \pm figures reported are average deviations.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WILLIAM M. RICE UNIVERSITY, HOUSTON, TEX.]

The Decomposition of Gaseous Chloroformates. I. The Rates of Simple Alkyl Compounds¹

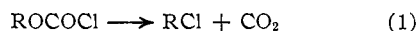
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The decompositions of some alkyl chloroformates near 250° in the gas phase are studied kinetically in a flow system. First-order rate constants for the formation of alkyl chloride and of olefins are determined. Some serious discrepancies with the literature on ethyl chloroformate exist, and are attributed to a possible heterogeneous reaction. A rather polar S_Ni mechanism is tentatively discussed.

Introduction

The thermal decomposition of alkyl chloroformates by reaction 1 has been considered to be an example of the S_Ni mechanism.² The basis of this



assignment was that there was clean retention of configuration on reaction of the pure liquid³ which is also observed in solution.⁴

The S_Ni mechanism was defined as a one-step unimolecular mechanism passing through a cyclic transition state. Studies of the reactions of the apparently analogous chlorosulfites, ROSOCl, led to the conclusion that the S_Ni picture was too simple, and that a carbonium ion or ion pair was intermediate. This satisfactorily explained a necessary solvent participation,⁵ neighboring group participation,^{6,7} secondary hydrogen isotope effects,⁸ as well as several qualitative arguments based on substituent effects.⁹ The analogy between chloroformates and chlorosulfites, originally based on the structural resemblance and the stereochemical course, is strengthened by the conclusion of Wiberg and Shryne⁴ (based upon a large negative Hammett rho) that the decomposition of substituted α -

phenylethyl chloroformates passed through a highly polar transition state.

The distinction between a highly polar transition state leading directly to neutral products and one leading to an ion pair is difficult. A clear distinction is possible if the ion pair is "solvent-separated"¹⁰ by the simple technique of using a gas phase system, thus eliminating the solvent. Naturally, a solvent-free ion pair in the gas phase can be expected to differ markedly from even an "intimate"¹⁰ ion pair in solution. Nevertheless, the non-chain gas phase pyrolyses of alkyl bromides show reactivities quite parallel to those in solvolytic reactions¹¹ and Ingold has gone to the extent of proposing ion pair intermediates for these reactions.¹²

The kinetics of the chloroformate reactions in the gas phase have been studied and a unimolecular reaction has been proposed. The rates and products reported in the literature are quite variable. The most thorough studies on ethyl chloroformate led to rate constants at 195°¹³ larger than that reported at 267° for the isobutyl ester,¹⁴ but comparable in rate to the isopropyl ester.¹⁵ At far more elevated temperatures ethylene has been identified as a reaction product as well as ethyl chloride from ethyl chloroformate¹⁶; the suggestion that rates were measurable is difficult

(1) From the Ph.D. Thesis of W. C. H., 1958, who thanks the National Science Foundation for a fellowship in 1954.

(2) W. A. Cowdrey, E. D. Hughes, C. K. Ingold, S. Masterman and A. D. Scott, *J. Chem. Soc.*, 1252 (1937); E. D. Hughes, C. K. Ingold and I. C. Whitfield, *Nature*, **147**, 206 (1941).

(3) A. H. J. Houssa and H. Phillips, *J. Chem. Soc.*, 108 (1932); 1232 (1932).

(4) K. B. Wiberg and T. M. Shryne, *J. Am. Chem. Soc.*, **77**, 2774 (1955).

(5) C. E. Boozer and E. S. Lewis, *ibid.*, **75**, 3182 (1953).

(6) D. J. Cram, *ibid.*, **75**, 332 (1953).

(7) H. J. Lucas and C. W. Gould, *ibid.*, **63**, 2541 (1941).

(8) C. E. Boozer and E. S. Lewis, *ibid.*, **76**, 794 (1954).

(9) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, N. Y., 1959.

(10) S. Winstein and G. C. Robinson, *J. Am. Chem. Soc.*, **80**, 1690 (1958).

(11) A. Macoll and P. J. Thomas, *Nature*, **176**, 392 (1955).

(12) C. K. Ingold, *Proc. Chem. Soc.*, 279 (1957).

(13) A. R. Choppin, H. A. Frediani and G. F. Kirby, Jr., *J. Am. Chem. Soc.*, **61**, 3176 (1939).

(14) E. T. Lessig, *J. Phys. Chem.*, **36**, 2325 (1932).

(15) A. R. Choppin and E. L. Compere, *J. Am. Chem. Soc.*, **70**, 3797 (1948).

(16) L. E. Roberts, R. Lashbrook, M. J. Treat and W. Yates, *ibid.*, **74**, 5787 (1952).

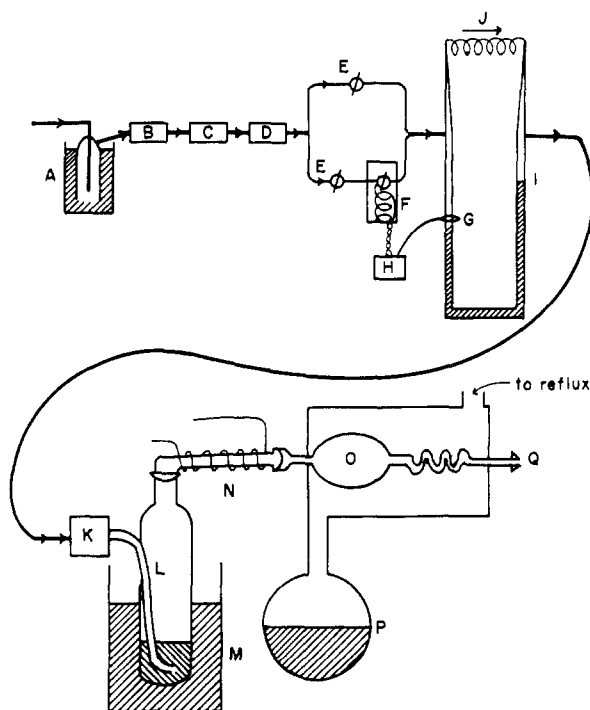


Fig. 1.—A, sulfuric acid pressure regulator; B, cold trap; C, K, drying tubes; D, hot combustion tube with copper turnings; E, needle valves; F, solenoid valve; G, external clip for capacity sensitive relay H on water manometer I, actuated by pressure drop through coiled capillary J; L, vaporizer containing liquid chloroformate, immersed in water-bath M; N, connecting tube electrically heated hotter than M; O, reaction vessel, heated by vapors of liquid boiling in P; Q, exit to analysis, cold trap or soap bubble flowmeter.

to reconcile with the Arrhenius parameters of reference 13, which predict a half-life of the order of one second at this temperature.

In this paper we attempt to resolve the kinetic discrepancies and show the rate variation with structural change in the alkyl group; in the following parts, the stereochemical course is studied and the rearrangement criterion for carbonium ions is applied.

Experimental

Materials.—Methyl, ethyl and phenyl chloroformates were commercially available; they were distilled and shown to be homogeneous by gas chromatography.

Isopropyl and *sec*-Butyl Chloroformates.—Tank phosgene was dissolved in a small amount of ether in a flask immersed in a Dry Ice-bath and equipped with a Dry Ice reflux condenser. One quarter of an equivalent of redistilled commercial isopropyl alcohol or *sec*-butyl alcohol, also dissolved in a small volume of ether, was added to the phosgene solution over a 3-hour period. The mixture was allowed to warm up overnight in the hood, the ether was removed at aspirator pressure, and the residue was distilled, b.p. 48–52° at 100 mm. for isopropyl chloroformate and b.p. 39–40° at 21 mm. for *sec*-butyl chloroformate. All chloroformates absorbed in the infrared at 5.60 μ .

Alkyl chlorides for comparison in gas chromatography were prepared in sufficient yield from the reaction of the corresponding alcohol with dry hydrogen chloride or Lucas reagent. Methyl chloride was also conveniently available for this purpose as a contaminant in a tank of methyl bromide. The isomeric butenes for comparison were obtained from the Phillips Petroleum Co.

Rate Measurements.—The reaction rate was measured by passing the chloroformate vapors into a heated vessel in a stream of nitrogen. The extent of reaction was determined by analysis of the effluent gas and the specific rates calculated from the extent of reaction and the flow rate. The flow apparatus is illustrated in block form in Fig. 1. Nitrogen from a tank was passed into a sulfuric acid pressure regulator, then through a drying train and a furnace with copper metal, to the flow control and metering device. Flow was controlled with a system of three valves, two in parallel were needle valves, and a solenoid valve in series with one needle valve was operated from a flowmeter which opened the valve when the flow rate was too small and closed it when the flow rate was too large. The gas flow through a capillary coil produced a pressure drop shown by a water manometer, and a detector clipped to the outside of the manometer operated a capacity sensitive Thermocap relay which operated the solenoid valve. Suitable adjustment of the needle valves allowed the flow rate to oscillate with small amplitude about the desired rate. This regulating system was followed by another drying tube.

The dry, oxygen-free, regulated stream then bubbled through the liquid chloroformate in a "vaporizer" immersed in a water-bath, the vapor-containing nitrogen passed through a short section of tubing, heated to prevent condensation, into the reaction vessel, the temperature of which was determined by a vapor jacket. The temperatures used were 240° (with *p*-anisidine), 255° (with biphenyl) and 279° (with α -bromonaphthalene). Only biphenyl was stable for long periods of reflux. The first vessel used had a volume of 100.3 ml., the second used for most of the experiments had a volume of 88.8 ml.; both were in the form of short cylinders with approximately hemispherical ends.

The effluent gas, containing the reaction products, was sampled for analysis by collection in a 10-ml. heated syringe, which was then used to put a sample into the gas chromatograph.¹⁷ Area measurements under the peaks were taken as proportional to the mole fraction, an assumption which was shown to be sufficiently good in several cases by the analysis of known mixtures. The peaks were identified by comparison of retention times with those of independently prepared samples, and in some cases also by the infrared spectrum of the vapor. When the effluent gas was passed through a cold trap and the condensate was analyzed, the results were non-reproducible, a difficulty we attribute to further reaction in the liquid phase, possibly catalyzed by hydrogen chloride. If methanol was added to the cold trap before collection of condensate, the extent of reaction given by the silver nitrate titer (which measures hydrogen chloride and chloroformate, but not alkyl chloride) agreed with the gas chromatographic results.

The effluent gas could also be passed into a buret through a soap solution, allowing the flow rate to be measured by the rate of passage of bubbles down the buret. Flow rate was measured either this way, or (less precisely) from the pressure drop in the regulating flow-meter, calibrated using a wet-test meter. A temperature correction was made.

Table I shows the results of six runs on the 2-butyl compound at 255°; the calculation of rate constants is described later. All the runs at this temperature using this analytical technique are included. The agreement between identical runs is somewhat better than the agreement between results of runs at varying conditions partly from systematic errors and partly from the usual improvement in details of technique which follows the repetition of an experiment. Results with other compounds are not shown in detail; they are comparable in nature. Runs on the methyl and ethyl compounds were carried to a much smaller extent of completion since the reaction is slower.

Demonstration of Mixing.¹⁸—Isooctane was placed in the vaporizer and the output of the reaction was connected to a gas sampling valve on the gas chromatograph. Flow was started and the gas was periodically sampled and analyzed for isooctane vapor. A plot of $\log(A_{\infty} - A_t)$ vs. t , where the A 's are the areas under the isooctane peak at various times t , was linear, and from the slope and the

(17) After completing this work, direct sampling in a gas sampling valve on the gas chromatograph was attempted by Mr. J. D. Allen. Except for complications introduced by condensation, the results were the same.

(18) We are indebted to Mr. J. D. Allen for this experiment.

TABLE I
 THE DECOMPOSITION OF 2-BUTYL CHLOROFORMATE AT 255°

Run no.	68	69	70	71 ^a	72 ^a	73 ^a
Flow rate, ml./sec.	0.0775	0.0775	0.255	0.104	0.103	0.104
Vaporizer temp., °C.	30	28	28	35	34	34
RCl, %	56.5	56.6	44.1	53.7	53.9	53.8
Butene-1, %	11.4	11.0	9.6	10.9	10.5	10.4
<i>trans</i> -Butene-2, %	11.0	10.8	8.0	10.8	10.6	10.2
<i>cis</i> -Butene-2, %	10.9	10.6	7.6	10.1	10.1	9.5
$k_8 \times 10^5 \text{ sec.}^{-1c}$	748	788	716	769	774	770
$k_1 \times 10^5 \text{ sec.}^{-1d}$	160	148	157	152	150	154
$k_t \times 10^5 \text{ sec.}^{-1e}$	156	145	130	150	152	151
$k_o \times 10^5 \text{ sec.}^{-1f}$	153	143	124	141	144	140
$\Sigma k \times 10^5 \text{ sec.}^{-1g}$	1216	1224	1127	1213	1220	1215

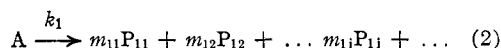
^a Interior of reaction vessel coated with Desiccote. ^b % of product is the % reaction by the indicated route; the difference between the sum of these and 100% represents unreacted chloroformate. ^c Rate constant for 2-chlorobutane. ^d Rate constant for butene-1. ^e Rate constant for *trans*-butene-2. ^f Rate constant for *cis*-butene-2. ^g Rate constant for disappearance of chloroformate, the sum of the preceding.

measured flow rate a volume of 90 ml. was calculated, which compares reasonably to the valve 88.8 ml. measured by the weight of water contained. This accuracy is within that of measurement and control of flow rate.

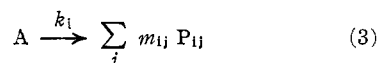
Results and Discussion

Although the determination of rate constants from the extent of reaction in a well-mixed flow system has been studied, the presence of a carrier gas and of parallel reaction paths introduces complexities which have not been treated.¹⁹ The derivations of the following equations are straightforward and are not given here.

Let us write that one mole of a reagent A yields by a first order process (with the rate constant k_1) m_{11} moles of the product P₁₁, m_{12} moles of P₁₂, etc., as shown in eq. 2. Let us assume that there



are several different modes of reaction with rate constants k_2, \dots, k_i, \dots all represented by eq. 3. If x_i is the fraction of the initial A which has re-



acted by path i , U is the flow rate of gas out of the reactor, U_0 is the flow rate in and V is the volume of the reactor, eq. 4 can be derived readily. Since

$$\sum_i k_i = \frac{U \sum_i x_i}{V(1 - \sum_i x_i)} \quad (4)$$

in a reaction such as 3 the number of molecules changes, $U \neq U_0$, and if U_0 is experimentally measured, eq. 5 is applicable, where N_A^0 is the mole fraction of A in the incoming gas stream. Equa-

$$\sum_i k_i = \frac{U_0}{V} \frac{\sum_i x_i}{(1 - \sum_i x_i)} \left(1 + \left[\sum_i \sum_j x_i m_{ij} - \sum_i x_i \right] N_A^0 \right) \quad (5)$$

tion 5 reduces to eq. 4 when N_A^0 is small or where $\sum x_i$ is small. In our experiments the two forms

(19) The most closely analogous systems are those of G. M. Harris, *J. Phys. Colloid Chem.*, **51**, 505 (1947).

were nearly indistinguishable. The individual rate constants, k_1 , can be calculated from eq. 6.²⁰

$$k_1 = \frac{x_1}{\sum_i x_i} \sum_i k_i \quad (6)$$

Equations analogous to 4 and 5 for equations of different order include important terms in N_A^0 ; thus the constancy of k_1 at different vaporizer temperatures and flow rates confirms the first-order nature of all the reactions. All our reactions appeared to follow this course.

Table II gives the rate constants calculated from the extents of reaction measured by gas chromatography and the flow rates. The random errors appear to be small, as is shown by the good agreement of essentially duplicate runs—for instance runs 71, 72 and 73 of Table I. Systematic errors

 TABLE II
 RATES OF DECOMPOSITION OF CHLOROFORMATES

R in ROCOCI	Temp., °C.	$\Sigma k_1 \times 10^5 \text{ sec.}^{-1a}$	Number of runs
CH ₃	240	0.533 ± 0.022 ^a	6
C ₂ H ₅	240	1.17 ± 0.08	11
C ₂ H ₅	240	2.70 ^b	1
C ₂ H ₅	255	2.99 ± 0.12	3
C ₂ H ₅	255	8.05 ^b	1
C ₂ H ₅	279	10.3 ± 0.2	3
<i>i</i> -C ₃ H ₇	240	232 ± 3	5
<i>i</i> -C ₃ H ₇	255	592 ± 29	5
2-C ₄ H ₉	240	501 ± 5	3
2-C ₄ H ₉	255	1203 ± 36	6
C ₆ H ₅	255	<0.1 ^c	3

^a Estimated errors are standard deviations from the mean of the number in the next column. ^b Not included in average; see text. ^c No significant reaction at the slowest flow rate practical.

in analysis are not serious, since known mixtures also in some cases were analyzed. Flow rate measurements using the bubble flowmeter are uncertain to the extent that the degree of solution of reaction products and chloroformate in the soap solution is not known. Since N_A^0 usually was small, this error is not serious. Flow rates were corrected to the reactor temperature using the ideal gas laws. Table II also includes two runs

(20) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 148.

not included in the average, with unusually rapid rates. These runs, both chronologically the first of a series, suggest the presence of a catalytic agent, probably a surface, which disappears on further reaction. Since an effort was made to attain a steady state before starting measurements, the initial rate may have been very rapid. Methyl and ethyl chloroformates gave no detected elimination products; isopropyl chloroformate and 2-butyl chloroformate both gave important amounts of olefin. Table III gives the average individual rates of formation of each product, with k_s defined as substitution reaction, that is, the rate of alkyl chloride formation, k_t the rate of 1-olefin formation, k_c the rate of *trans*-butene-2 formation, and k_e that for *cis*-butene-2.

TABLE III
INDIVIDUAL RATES OF DIFFERENT ROUTES FROM SECONDARY CHLOROFORMATES

R in ROCOCI	Temp., °C.	k_t	$\frac{-10^3 \text{ sec.} \times}{k_c}$		k_s
<i>i</i> -C ₃ H ₇	240	112			120
<i>i</i> -C ₃ H ₇	255	334			258
2-C ₄ H ₉	240	64.2	48.2	45.8	343
2-C ₄ H ₉	255	154	147	141	761

These data can be used with the Eyring equation to calculate heats and entropies of activation. Since the olefin distribution is not markedly temperature sensitive, the total elimination reaction is given for the 2-butyl compound in Table IV. The error estimates are crudely based upon the errors in Table II and III.

TABLE IV
ACTIVATION PARAMETERS FOR CHLOROFORMATES

Compound	ΔH^* , kcal./mole ± 1		$-\Delta S^*$, e.u. ± 2	
	Subst.	Elim.	Subst.	Elim.
Ethyl	36.7		-21	
Isopropyl	26.2	37.2	-22	+1
2-Butyl	27.8	35.9	-17	-1

No conceivable errors can bring these data for the ethyl compound into agreement with those of Choppin, Frediani and Kirby.¹³ Their data give $\Delta H^* = 28$ kcal./mole, $\Delta S^* = -18$ e.u., which leads to a predicted rate at 240° of 0.015 sec.⁻¹, about 1300 times our rate. Similarly, extrapolating with Table IV, we would predict a rate at their temperatures about 10⁻⁴ times theirs. Our rates for the ethyl compound are more nearly comparable to Lessig's value for isobutyl chloroformate; $k = 7.2 \times 10^{-4}$ sec.⁻¹ at 267°.¹⁴

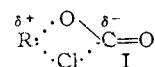
The only reasonable source of a discrepancy of this magnitude is that a mechanism exists which is variable in rate, such as a catalysis by foreign substances. Choppin and Kirby²¹ were unable to find any substantial effect of a variety of added substances, including packing with ground glass, glass wool or quartz. In spite of these experiments a surface catalysis appears the most probable source of the discrepancy. The failure to find surface effects may possibly be attributed to a difference in washing techniques for the vessel, which was

(21) A. R. Choppin and G. F. Kirby, Jr., *J. Am. Chem. Soc.*, **62**, 1592 (1940).

washed in the acid, and the packing, the cleaning of which is not described. Surface effects were observed with the isopropyl compound.¹⁵ On independent grounds, Benson²² has suggested the possibility of heterogeneity in these results. The absence of surface effects cannot be demonstrated in our experiments, but the conditions are more conducive to a homogeneous reaction, since adsorption is reduced by the higher temperature and the low partial pressures of chloroformate, and the poisoning of reactive centers of seasoning can be more complete in a flow system, since measurements were only made after many hours of reaction in order to achieve the steady state. No significant changes on coating the vessel with the silicone material Desiccote were observed, as can be seen from Table I. The possibility that a very large initial rate existed for ethyl chloroformate has been mentioned in connection with two runs shown in Table II.

The report of ethylene as a product of ethyl chloroformate decomposition¹⁶ is not incompatible with our results. Our evidence for the absence of ethylene rests only on the observation that ethyl chloride accounted for the missing ethyl chloroformate. A few per cent. of ethylene would not have caused a serious discrepancy. Furthermore, Table IV shows that the elimination reaction in the secondary compounds has a higher activation energy than substitution. If this can be extended to the ethyl compound, then ethylene would become increasingly important at higher temperatures, such as in the 300–330° range studied by Roberts.

The relative reaction rates at 240°, CH₃ = 1, C₂H₅ = 2.2, *i*-C₃H₇ = 220, 2-C₄H₉ = 640, illustrates the acceleration by α -alkyl substitution, also characteristic of the inhibited homogeneous elimination of alkyl bromides¹¹ and the solvolysis of alkyl halides. The obvious extension to the *t*-butyl compound was made impractical since this substance decomposes at room temperature in the liquid phase.²³ If we follow Macoll and Thomas¹¹ and Ingold¹² and assume a rather polar transition state with the rough structure I, the low reactivity



of trichloromethyl chloroformate, which decomposes more slowly to different products,²⁴ may be attributed to the low stability expected of I with R = -CCl₃. A simple ion pair without the constraints of I is excluded for the substitution reaction because of the large negative entropy of activation, but is not excluded for the elimination reaction. The unreactivity of phenyl chloroformate can be understood both in terms of the unfavorable nature of the phenyl cation and the stronger carbon-oxygen bond expected from resonance.

(22) S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p. 259, footnote 7.

(23) A. R. Choppin and J. W. Rogers, *J. Am. Chem. Soc.*, **70**, 2967 (1948).

(24) H. C. Ramsberger and G. Waddington, *ibid.*, **55**, 214 (1933).