728. *The Mechanism of Hydrolysis of Acid Chlorides. Part VII.* Alkyl Chloroformates.*

By E. W. Crunden and R. F. Hudson.

A kinetic study of the solvolysis of methyl, ethyl, and isopropyl chloroformate in formic acid and in aqueous acetone is reported.

The change in order of reactivity is attributed to a change in mechanism from a bimolecular displacement at the carbonyl group to an ionisation. In formic acid, (+)-1-methylheptyl chloroformate solvolyses with almost complete inversion of configuration, showing that alkyl–oxygen fission occurs at some stage of the reaction. The present results do not prove whether rate-determining alkyl–oxygen or acyl–chlorine fission occurs.

As part of a detailed study of the mechanism of solvolysis of acid chlorides, we have investigated kinetically the reaction of several aliphatic chloroformates in formic acid solution and in aqueous acetone. As a chloroformate contains an ester group in addition to the acyl chloride group, both acyl–oxygen and alkyl–oxygen fission have to be considered in addition to heterolysis of the carbon–chlorine bond. Each bond fission could conceivably occur by bimolecular displacement or by an ionisation mechanism, and hence the operative reaction mechanism is likely to be particularly difficult to establish.

There are few quantitative data available on the replacement reactions of chloroformates, apart from the effect of structure on the rate of methanolysis.[1] This reaction leads to a mixed carbonate ester: $RO{\cdot}COCl + MeOH \longrightarrow RO{\cdot}CO_2Me + HCl$

The following order shows that the reactivity is reduced by electron release to the carbonyl-carbon atom, which increases conjugation in the ground state ($R{\rightarrow}O\underset{\cdots}{-}C\underset{\cdots}{-}O{\cdot}Cl$): $Cl{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}COCl > MeO{\cdot}COCl > EtO{\cdot}COCl > Pr^iO{\cdot}COCl$. The reaction may therefore be assumed to proceed by bimolecular displacement at the carbonyl group.

In aqueous solution, ethyl chloroformate gives alcohol and hydrochloric acid, although

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* Part VI, *J.*, 1956, 501.

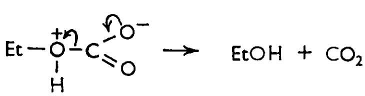
[1] Leimu, *Ber.*, 1937, **70**, 1040.

at 100° some ethylene is obtained.[2] The hydrolysis is strongly catalysed by sodium hydroxide [3] and is thought to proceed by bimolecular displacement to give the monoalkyl carbonate, which decomposes rapidly in acid or neutral solution [4] to give the alcohol:

$$\mathrm{EtO{\cdot}COCl} + \mathrm{H_2O} \longrightarrow \mathrm{EtO{\cdot}CO_2H} + \mathrm{HCl}$$

$$\mathrm{EtO{\cdot}CO_2H} \rightleftharpoons \mathrm{{}^{+}HEtO{\cdot}CO_2{}^{-}} \longrightarrow \mathrm{EtOH} + \mathrm{CO_2}$$

The second stage is known to proceed with retention of configuration,[5] supporting the following mechanism:



In agreement with the bimolecular mechanism, we find that methyl chloroformate is more reactive than ethyl chloroformate in a 65 : 35 v/v mixture of water and acetone (Table 1). The predominantly bimolecular nature of the reaction of ethyl chloroformate in aqueous acetone is further indicated by the pronounced effect of added hydroxide ions on the rate † (Table 2). However, Table 1 shows that isopropyl chloroformate is more reactive than the ethyl ester, suggesting a change in mechanism to an ionisation process. Moreover, chloroformates of tertiary alcohols are extremely unstable [6] and rearrange rapidly at room temperature, probably through the intermediate formation of a carbonium ion.

TABLE 1. *Solvolysis of alkyl chloroformates in formic acid and in* 65% *aqueous acetone at* 50°.

	Formic acid, 1% water: 10^5k (sec.$^{-1}$)	65% Acetone: 10^5k (sec.$^{-1}$)	Activation energy in formic acid (kcal. mole^{-1})	k (aq. $\mathrm{COMe_2}$)/ k ($\mathrm{H{\cdot}CO_2H}$)
MeO·COCl	0·103	242	—	2350
EtO·COCl	7·67	109	25·1	14
Pr^{i}O·COCl	540	760	22·7	1·4

TABLE 2. *Effect of ammonium hydroxide on the solvolysis of ethyl chloroformate in aqueous acetone at* 0°.

$\mathrm{H_2O}$ (%)	Concn. of chloroformate (M)	Concn. of hydroxide (M)	$k_2(\mathrm{OH^-})$ (l. mole^{-1} min.$^{-1}$)	$\dfrac{k_2(\mathrm{OH^-})}{k_2(\mathrm{H_2O})}$
18	0·0286	0·0286	168	$3{\cdot}05 \times 10^7$
85	0·0286	0·0286	153	$3{\cdot}44 \times 10^6$

In order to study the ionisation process, the reactions were examined in more detail in formic acid, which is known to suppress bimolecular nucleophilic reactions.[7] The irreversible nature of the reaction in this solvent was confirmed by showing that the conductivity at the end of the solvolysis was equal to that of a solution containing an equivalent amount of hydrochloric acid. The effect on the rate of formolysis of increasing the water concentration has been determined at three temperatures for ethyl chloroformate and at 50° for isopropyl chloroformate. In all cases the changes are small over the 0—5% water-concentration range (for details see Table 6), showing that the reaction

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† Results obtained by Dr. B. Saville.

[2] Thiele and Dent, *Annalen*, 1898, **302**, 256.

[3] Hall, *J. Amer. Chem. Soc.*, 1955, **77**, 5993.

[4] Faurholt and Gjaldbaek, *Dansk Tidsskr. Farm.*, 1945, **19**, 255; and previous papers.

[5] Garner and Lucas, *J. Amer. Chem. Soc.*, 1950, **72**, 5497.

[6] Choppin and Rogers, *J. Amer. Chem. Soc.*, 1948, **70**, 2967.

[7] Bateman, Hughes, Ingold, and Taher, *J.*, 1940, 979.

is insensitive to the addition of a more nucleophilic reagent. We have previously demonstrated [8] that the rate of reaction of *p*-nitrobenzoyl chloride, which proceeds by a bimolecular mechanism, is proportional to the water concentration in formic acid.

In the present case there is a slight decrease in rate with increasing water content, to give a minimum at 4%; this we attribute to a change in the properties of the medium produced by the strong acid–base interaction between water and formic acid, $H_2O + H{\cdot}CO_2H \rightleftharpoons H_2O \cdots HO_2C{\cdot}H$, which effectively reduces the concentration of formic acid available for solvation. If this equilibrium is assumed to go to completion, the fractional decrease in rate is of a similar magnitude to the decrease in the mole fraction of " free " formic acid (Table 3). t-Butyl chloride has been found to behave in a similar way.[9] The rate of formolysis of t-butyl chloride is approximately constant over the 0—10% water-concentration range in accordance with its S_N1 mechanism. However, there is again a slight decrease in rate, and as in the case of the chloroformates the fractional change in rate is of the same order of magnitude as the decrease in mole fraction of the " free " formic acid (Table 3). The similar behaviour of t-butyl chloride and ethyl chloroformate supports the contention that the latter reacts in formic acid by an ionisation mechanism.

TABLE 3. *The change in the rate of formolysis with the mole fraction of " free " formic acid* ($*H{\cdot}CO_2H$).

		Cl·CO₂Et, 10^5k (sec.$^{-1}$)						Bu^{t}Cl			
H_2O (%)	$*H{\cdot}CO_2H$		at 50°		60°		70·2°		H_2O (%)	$*H{\cdot}CO_2H$		10^5k (sec.$^{-1}$) at 0°	
0·97	0·978	dec. 7%	7·76	dec. 6%	24·0	dec. 5%	75·2	dec. 7%					
1·76	0·955		7·56		—		—		1·0	0·964	dec. 10%	39·8	dec. 8%
2·95	0·930		7·34		—		—		2·0	0·938		37·0	
3·74	0·912		7·34		22·8		70·1		5·0	0·854		36·6	
8·90	0·800		8·22		25·2		72·4		10·0	0·770		35·3	

As the concentration of water increases above 4% (v/v), the rate gradually increases owing to the incursion of the bimolecular reaction which proceeds in aqueous solution.

Similarly the addition of sodium formate produces small rate increases (Table 4), which are attributed to the bimolecular displacement, $Cl{\cdot}CO_2Et + H{\cdot}CO_2^- \longrightarrow EtO_2C{\cdot}O{\cdot}COH + Cl^-$, which occurs together with the solvolytic ionisation process. The rate increases are small compared with those observed in the corresponding reaction of *p*-nitrobenzoyl chloride.[8] There the addition of 0·023N-sodium formate increased the initial rate of reaction in 1·4% aqueous formic acid by approximately one-thousand fold. This increase is to be compared with the increase of *ca.* 27% for ethyl chloroformate and *ca.* 7% for isopropyl chloroformate in 2·74% aqueous formic acid on the addition of 0·033N-sodium formate. We conclude therefore that, although added formate ions may participate in a bimolecular displacement reaction, at least with ethyl chloroformate, the solvolysis in formic acid proceeds by an ionisation process.

TABLE 4. *Effect of sodium formate on the rate of formolysis of ethyl and isopropyl chloroformate at* 50°.

Compound	H_2O (%)	$Cl{\cdot}CO_2R$ (mole/l.)	Formate (mole/l.)	$10^5k(H{\cdot}CO_2^-)$ (sec.$^{-1}$)	10^5k (solv.) (sec.$^{-1}$)
$Cl{\cdot}CO_2Et$	2·78	0·0171	0·0336	9·23	7·34
,, ...	2·78	0·0196	0·0336	9·46	7·34
,, ...	2·94	0·0209	0·1235	13·7	7·34
,, ...	5·7	0·0137	0·0840	14·0	7·6
,, ...	10·9	0·0286	0·0840	17·25	9·0
$Cl{\cdot}CO_2Pr^i$	2·78	0·00896	0·0336	569	530

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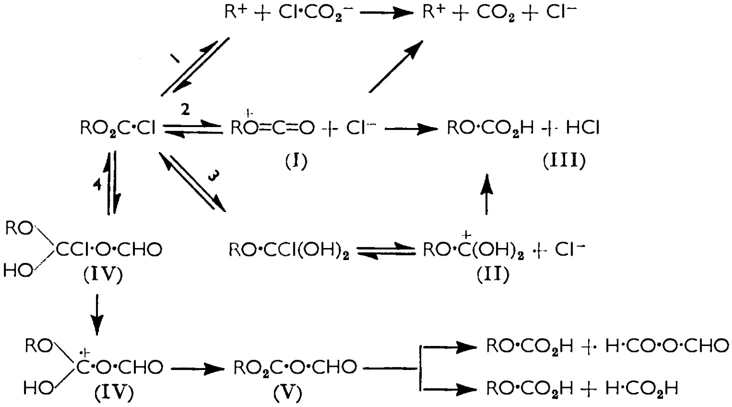
[8] Crunden and Hudson, *J.*, 1956, 501.

[9] Bateman and Hughes, *J.*, 1937, 1187.

It is now necessary to consider the nature of this process in more detail. Tables 1 and 6 show that the rate increases rapidly with electron-release to the reaction centre. The rate ratios given in Table 1 are similar to those found for the formolysis of alkyl sulphonate esters,[10] which are known to form carbonium ions under such conditions. The rate data, therefore, agree with the assumption of a rate-determining heterolysis of the alkyl–oxygen bond (1).



Other mechanisms, are, however possible. Thus a rate-determining ionisation of the C–Cl bond may give an acylium ion (I), stabilised by conjugation with the lone-pair electrons of the alkoxy-oxygen atom. Since electron-release from R decreases the ionisation potential of these electrons, the conjugation energy is increased and the observed reactivity thus increased. An ion of this kind may behave as an acylating agent and react with water to give the alkyl hydrogen carbonate (III), or with formic acid to give the anhydride, or as an alkylating agent to give the alcohol or corresponding formate.

Alternatively, addition of water (3) or formic acid (4) may give the diol or orthoester (IV), respectively, which then undergo rate-determinging ionisation to give the carbonium ions (II) and (VI) respectively. Although the first stage of each reaction is retarded by increased conjugation in the chloroformate, the second stage is assisted by electron-release from R. Conjugation in ions (II) and (VI) may be greater than in the corresponding ground states owing to the decrease in electron density on the carbon atom. Substitution by electron-releasing groups in R may, therefore, lead to an increase in reactivity. A similar explanation of the ionisation mechanism of acyl chlorides has been advanced by Hall.[3]

The intermediate (II) would eliminate a proton to give the alkyl hydrogen carbonate, which rapidly decomposes under acid conditions, to give alcohol and carbon dioxide.[4] Since this reaction proceeds with retention of configuration of the alcohol, this mechanism may be rejected because at least 95% inversion is observed during the solvolysis. Similarly the mixed anhydride (V) produced by preliminary addition of formic acid is known to be highly unstable [11] and may decompose by several routes. Thus the typical acid-catalysed hydrolysis or formolysis of an anhydride would again lead to the alkyl hydrogen carbonate, resulting in retention of configuration of the alcohol.

Alternatively the decomposition may be intramolecular,[12] since unsymmetrical anhydrides of this kind have been found to decompose rapidly at room temperature in inert solvents. The mechanism has not been fully established, but the reactivity appears to be increased by electron-release in the alkyl ester group and by electron-withdrawal

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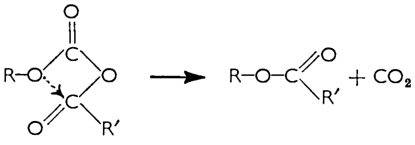
[10] Winstein and Marshall, *J. Amer. Chem. Soc.*, 1952, **74**, 1120.

[11] Tarbell and Longosz, *J. Org. Chem.*, 1959, **24**, 774; Tarbell and Leister, *ibid.*, 1958, **23**, 1149.

[12] Boschan, *J. Amer. Chem. Soc.*, 1959, **81**, 3341; Windholtz, *J. Org. Chem.*, 1960, **25**, 1703.

from the carbonyl group of the carboxylic acid. The decomposition also proceeds with retention of configuration,[11] in agreement with the mechanism:



These considerations suggest that the mixed anhydride is not formed in the solvolysis, leaving mechanisms (1) and (2) as the most likely. The former is preferred since S_N1 ionisation of the C–O bond of esters normally leads to a high degree of racemisation in formic acid. Thus experiments showed that (+)-1-methylheptyl methanesulphonate gave a completely racemised formate on solvolysis in formic acid under conditions where the alcohol was unaffected.* This suggests that a free carbonium ion is formed in the solvolysis of sulphonates but not in the solvolysis of secondary chloroformates. Further work is in progress in an attempt to determine the nature of this reaction mechanism.

EXPERIMENTAL

Materials.—With the exception of ethyl chloroformate, each chloroformate was prepared by passing an excess of carbonyl chloride into a solution of the corresponding alcohol in dry ether [13] cooled in acetone–carbon dioxide. The mixture was left at room temperature for 24 hr., and the ether and hydrogen chloride were then removed under reduced pressure. The remaining liquid was fractionally distilled. Thus were obtained: methyl, b. p. 69—70°, n_D^{21} 1·3865 (lit.,[14] b. p. 71—72° n_D^{20} 1·3868), ethyl, b. p. 94°, isopropyl, b. p. 104—105° (lit.,[15] b. p. 101—102°/745 mm.), neopentyl, b. p. 54—56°/36 mm., n_D^{20} 1·4090 (lit.,[13] n_D^{25} 1·4073), and (+)-1-methylheptyl chloroformate, $[\alpha]_D^{22\cdot5}$ + 24·0° (lit.,[17] $[\alpha]_D^{19}$ + 23·78°) (from the alcohol, $[\alpha]_D^{22\cdot5}$ + 9·25°), same b. p. and n_D as the (±)-product, b. p. 60—61°/5 mm., n_D^{17} 1·4289 (lit.,[17] b. p. 92°/13 mm., n_D^{20} 1·4282).

Neopentyl alcohol was prepared by Nystrom and Brown's method.[16]

(—)-1-Methylheptyl formate was prepared by the action of formic acid on the (+)-alcohol in the presence of zinc chloride [18] and had b. p. 81°/20 mm., $[\alpha]_D^{20}$ —4·16° (lit.,[18] b. p. 81—82°/20 mm., $[\alpha]_D^{20}$ —4·16°).

Formic acid (" AnalaR " containing 1—2% of water) was used without further purification. The water content of each batch was determined by the Karl Fischer method,[19] and standard solutions were made by adding weighed amounts of water.

The water concentration was obtained from a calibration graph relating concentration to conductivity.

Acetone (" AnalaR ") was left overnight with potassium carbonate. Phosphoric oxide was added to the decanted liquid which was then distilled with a reflux ratio of 20 : 1 through a 50-cm. column packed with Fenske helices; it had b. p. 56·5°.

Dioxan was refluxed with N-hydrochloric acid for 8 hr. in a stream of nitrogen, then treated with pellets of sodium hydroxide and separated from the aqueous layer. The liquid was stored over sodium wire for several days and fractionally distilled from sodium (b. p. 101°).

Products.—A flask containing formic acid (50 ml.) was immersed in a thermostat bath and connected to two traps immersed in acetone–carbon dioxide; the traps were connected to a bubbler containing N-potassium hydroxide (50 ml.) and then to one containing saturated barium hydroxide solution (50 ml.). The air in the apparatus was displaced with nitrogen

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* Personal communication from Dr. R. Deitz.

[13] Wiberg and Shryne, *J. Amer. Chem. Soc.*, 1955, **77**, 2774.
[14] Thiele and Dent. *Annalen*, 1898, **302**, 269.
[15] Hamilton and Sly, *J. Amer. Chem. Soc.*, 1925, **47**, 437.
[16] Nystrom and Brown, *J. Amer. Chem. Soc.*, 1947, **69**, 2548.
[17] Hunter, *J.*, 1924, **125**, 1389.
[18] Pickard, Kenyon, and Hunter, *J.*, 1923, **123**, 10.
[19] Karl Fischer, *Angew. Chem.*, 1935, **48**, 394.

before the bubblers were connected, and then a slow stream of nitrogen was passed through for 2 hr. The concentration of the potassium hydroxide solution remained constant, showing that all the formic acid vapour was removed from the nitrogen stream.

A weighed amount (1·04 g.) of isopropyl chloroformate was added to the formic acid, and the slow nitrogen stream continued for a sufficient time to displace the carbon dioxide formed. The potassium hydroxide solution was then analysed for carbonate by titration with N-sulphuric acid to phenolphthalein and Methyl Orange, with the following results: 98% of CO_2 in 6·5 hr. at 25°; 100% of CO_2 in 40 min. at 50° (99% in 1 hr.). The quantitative formation of carbon dioxide and the production of one equivalent of hydrochloric acid per mole of chloroformate show that the following reaction occurs quantitatively in dilute solution: $Cl{\cdot}CO_2R + H{\cdot}CO_2H \longrightarrow H{\cdot}CO_2R + CO_2 + HCl$.

Measurement of Rate Constants.—Most of the measurements were made conductimetrically by the method described previously.[8]

(a) *Solvolysis.* The required solvent (50 ml.) was raised and lowered in the upper part of the cell several times, and then allowed to acquire the temperature of the thermostat. The compound to be solvolysed was added, and the cell shaken until dissolution was complete. The liquid was then raised into the upper part of the cell and, after several minutes for equilibration, conductivity readings were taken at regular intervals. A typical experiment is recorded in Table 5 (*R* in ohms).

TABLE 5. *Solvolysis of ethyl chloroformate* (0·0376N) *in formic acid containing* 1·76% *of water, at* 50°.

t (min.)	R_t	$\log [R_t/(R_t - R_\infty)]$	t (min.)	R_t	$\log [R_t/(R_t - R_\infty)]$	t (min.)	R_t	$\log [R_t/(R_t - R_\infty)]$
0	31,160	0·0607	122	8770	0·2788	195	6686	0·4216
65	13,290	0·1644	131	8386	0·2967	205	6508	0·4425
83	11,460	0·1959	151	7715	0·3345	217	6327	0·4654
91	10,780	0·2122	162	7404	0·3579	227	6186	0·4829
101	10,080	0·2330	172	7163	0·3766	246	5940	0·5211
112	9242	0·2377	179	7012	0·3892	256	5834	0·5416
						∞	4155	—

$k_1 = 7{\cdot}56 \times 10^{-5}$ sec.$^{-1}$. $t_{\frac{1}{2}} = 153$ min.

For calibration, a known weight of ethyl chloroformate was weighed into the solvent and allowed to solvolyse to completion. The conductivity was recorded of this solution and of solutions derived from it by successive dilutions. In all cases the conductivity was proportional to the concentration over the range employed (0·005—0·05M), and the rate constants were calculated by assuming the reaction to be of the first order.

A summary of the results obtained with several chloroformates and varying amounts of water in the formic acid is given in Table 6. For comparison, similar rate constants obtained in a solvent containing water 65% and acetone 35% (by volume) are given in Table 7.

Reactions in the Presence of Formate or Chloride Ions.—Standard sodium hydroxide solution was added to formic acid of known water content, to form a known amount of sodium formate. The extra water added in this way is included in the total water concentration recorded in Tables 9 and 10.

The experimental procedure was as for the solvolysis. The resistance of the solution increased as the reaction proceeded, showing that formate ions are replaced by less strongly conducting chloride ions. The accelerating effect of the formate ions was small, and good first-order plots were obtained as before. Instead of the function $\log_{10} [R_t/(R_t - R_\infty)]$, the function $\log_{10} [R_t/(R_\infty - R_t)]$ was plotted against t. The validity of this method has been demonstrated previously,[8] and a typical run is given in Table 8.

In the presence of sodium chloride, the resistance of the solution decreased, and the rate constant was calculated as for the solvolysis experiments.

The salt-effect experiments for ethyl and isopropyl chloroformate are recorded in Tables 9 and 10.

Optical-activity Experiments.—Measurements of optical rotation were made with a Hilger " Microptic " polarimeter with a sodium lamp. The apparatus was enclosed in an air-thermostat (±0·1°), and the rotation could be measured within ±0·01°.

Since the specific rotation varies with the solvent, (+)-1-methylheptyl formate was examined in formic acid ($[\alpha]_D^{20}$ −7·92° at 20°), and in formic acid containing 10% of dioxan (α_D^{20} −8·06° at 20°) to increase solubility.

TABLE 6. *Hydrolyses in formic acid.*

$Cl{\cdot}CO_2R$ (M)	Temp.	H_2O (% v/v)	10^5k (sec.$^{-1}$)	$Cl{\cdot}CO_2R$ (M)	Temp.	H_2O (% v/v)	10^5k (sec.$^{-1}$)
	R = Ethyl				R = Methyl		
0·0314	50·0°	0·97	7·67	0·0139	50·0°	0·74	0·108
0·0348	50·0	0·97	7·86	0·0139	50·0	0·74	0·099
0·0376	50·0	1·76	7·56				
0·0282	50·0	2·95	7·34		R = Neopentyl		
0·0334	50·0	3·74	7·34	0·00685	25·0	0·74	0·250
0·0248	50·0	4·94	7·36				
0·0427	50·0	6·90	7·86		R = Isopropyl		
0·0292	50·0	8·90	8·22	0·0196	25·3	0·74	29·2
0·0144	60·0	0·97	24·0	0·0117	33·0	0·74	71·5
0·0208	60·0	3·74	22·8	0·0214	50·0	0·97	539
0·0256	60·0	8·90	25·2	0·0177	49·9	2·97	530
0·0125	70·2	0·97	75·2	0·0203	50·0	6·90	579
0·0168	70·2	3·74	70·1				
0·0364	70·2	8·90	72·4		R = 1-Methylheptyl		
				0·01075	25·0	0·74	37·2
				0·00702	33·0	0·74	95·8
				0·00507	50·0	0·74	669

TABLE 7. *Hydrolysis in water* 65% *and acetone* 35% (*v/v*) *at* 50°.

$Cl{\cdot}CO_2R$: R	Me	Et	Pr^i
[$Cl{\cdot}CO_2R$] (M)	0·0102	0·0100	0·0189
10^5k (sec.$^{-1}$)	242	109	760

TABLE 8. *Hydrolysis of ethyl chloroformate* (0·0171M) *in formic acid containing sodium formate* (0·0336M) *and water* (2·78% v/v) *at* 50·0°.

t (min.)	R_t	$\log_{10}[R_t/(R_\infty - R_t)]$	10^5k (sec.$^{-1}$)	t (min.)	R_t	$\log_{10}[R_t/(R_\infty - R_t)]$	10^5k (sec.$^{-1}$)
0	3070·0	0·7024	—	150	3395·0	1·0755	9·53
18	3121·5	0·7482	9·76	263	3522·0	1·3502	9·45
20	3126·5	0·7528	9·67	297	3547·0	1·4281	9·38
42	3187·0	0·8116	9·98	321	3562·5	1·4829	9·33
57	3223·0	0·8482	9·82	341	3573·5	1·5276	9·29
89	3292·0	0·9284	9·74	372	3589·5	1·6010	9·27
100	3313·0	0·9557	9·72	∞	3679·5	—	—
120	3350·0	1·0060	9·71				

k (obtained graphically) = 9·23 × 10^{-5} sec.$^{-1}$. $t_{\frac{1}{2}}$ = 125 min.

TABLE 9. *Salt effect for ethyl chloroformate at* 50°.

$Cl{\cdot}CO_2Et$ (M)	Salt (N)	H_2O (% v/v)	10^5k_1 (sec.$^{-1}$)	$Cl{\cdot}CO_2Et$ (M)	Salt (N)	H_2O (% v/v)	10^5k_1 (sec.$^{-1}$)
0·0354	0·051 NaCl	0·74	6·94	0·0209	0·1235 $H{\cdot}CO_2Na$	2·94	13·7
0·0171	0·0336 $H{\cdot}CO_2Na$	2·78	9·23	0·0137	0·0840 ,,	5·90	14·0
0·0196	0·0336 ,,	2·78	9·46	0·0286	0·0840 ,,	10·9	17·25

TABLE 10. *Salt effect for isopropyl chloroformate at* 49·9°.

$Cl{\cdot}CO_2Pr^i$ (M)	Salt (N)	H_2O (% v/v)	10^5k (sec.$^{-1}$)
0·0231	0·051 NaCl	0·74	557
0·0131	0·102 ,,	0·74	525
0·00896	0·0336 $H{\cdot}CO_2Na$	2·78	569

(i) *Esterification of* (+)-1-*methylheptanol in formic acid.* (*a*) A solution of the alcohol (3·198 g.) in 98% formic acid (100 ml.) at 21° gave a constant rotation of −0·16° ± 0·01° (0·5 dm. tube) within 1 hr. Complete conversion into the formate being assumed, the specific rotation of the formate is $[\alpha]_D^{21}$ −8·2° ± 0·5°, in agreement with the values obtained after solvolysis (Table 11).

TABLE 11. *Final values for reaction of ethyl chloroformate with formic acid.*

Temp.	Chloroformate (%)	Formate (%)	Tube (dm.)	α	$[\alpha]_D$
17·5°	1·60	1·31	4	+0·46°	+8·8°
22·5	2·06	1·69	2	+0·27	+8·0

(*b*) A 0·014M-solution of acetyl chloride in 98% formic acid was kept for a few minutes to allow complete solvolysis to take place. The alcohol (6·16 g.) was added to this solution (100 ml.), and the final rotation of −1·25° ± 0·01° (2 dm. tube) was measured. This gives $[\alpha]_D^{21}$ −8·4° ± 0·1° for the formate, showing that hydrochloric acid has no effect on the esterification.

(*c*) The esterification was repeated in a mixture of 90% of formic acid (98%) and 10% of dioxan (v/v), 0·046M in hydrochloric acid produced from acetyl chloride as described above. A 9·84% solution of the alcohol gave a constant rotation of −1·60° ± 0·01° (2 dm. tube). If conversion is complete, the formate has $[\alpha]_D^{21}$ −8·1° ± 0·05° (cf. $[\alpha]_D^{21}$ −7·90° for this formate in formic acid).

(ii) *Inversion of* (+)-1-*methylheptyl chloroformate in formic acid.* A 1·36% solution of the chloroformate in formic acid (98%) at 21° gave a final constant reading of +0·19° ± 0·01° in a 2 dm. tube. If the reaction $\mathrm{Cl{\cdot}CO{\cdot}OC_8H_{17} + H{\cdot}CO_2H \longrightarrow H{\cdot}CO{\cdot}OC_8H_{17} + HCl + CO_2}$ goes to completion, the specific rotation of the formate is calculated to be $[\alpha]_D^{21}$ +8·5° ± 0·4° (cf. $[\alpha]_D^{20}$ −8·1° for this formate in formic acid).

In the following experiments the change in specific rotation with time was measured, and by assuming complete conversion of the chloroformate into formate, the rate constant for the solvolysis was obtained. The final rotations and specific rotations, calculated on the basis of complete conversion, are recorded in Table 11. The mean value of $[\alpha]_D$ +8·4° ± 0·4° indicates that (+)-1-methylheptyl chloroformate is converted almost entirely into (−)-1-methylheptyl formate. In Table 12 typical data for a kinetic measurement are recorded.

TABLE 12. *Rate of hydrolysis of* (+)-1-*methylheptyl chloroformate* (0·0832M) *in formic acid containing* 10% *of dioxan and* 0·74% *of water at* 17·5°.

t (min.)	α_t	$1 + \log_{10} [\alpha_\infty/(\alpha_t - \alpha_\infty)]$	*t* (min.)	α_t	$1 + \log_{10} [\alpha_\infty/(\alpha_t - \alpha_\infty)$	*t* (min.)	α_t	$1 + \log_{10} [\alpha_\infty/(\alpha_t - \alpha_\infty)]$
0	—		135	+0·96°	0·9638	253	+0·75°	1·2014
34	+1·23°	0·7767	150	+0·92	1·0000	286	+0·71	1·2648
64	+1·14	0·8306	175	+0·86	1·0607	330	+0·67	1·3404
75	+1·10	0·8567	217	+0·79	1·1430	∞	+0·46	—
109	+1·03	0·9074						

4 dcm. polarimeter tube; $k = 7{\cdot}49 \times 10^{-5}$ sec.$^{-1}$. The rate constant, k_1, was calculated from the first-order rate equation, $\log\{\alpha_\infty/(\alpha_t - \alpha_\infty)\} = k_1 t/2{\cdot}303$ + constant, where α_t is the observed rotation at time *t* and α_∞ is the final rotation.

The rate constants for several similar experiments are recorded in Table 3. The water content was 0·74%, reference being to that of the formic acid, not of the dioxan–formic acid mixture.

TABLE 13. *Various rate constants* (*see text*).

$\mathrm{Cl{\cdot}CO{\cdot}OC_8H_{17}}$ (M)	0·00948	0·0832	0·1195	0·1070
Temp.	25°	17·5°	17·5°	22·5°
$10^5 k_1$ (sec.$^{-1}$)	20·8 *	7·49	7·29	16·4

* Conductimetric estimation.

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