

233. *Pyrolyses of Some t-Butyl Derivatives.*

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Thermal decompositions of t-butyl chloroacetate and dichloroacetate have been observed to be homogeneous in a seasoned Pyrex vessel and follow the unimolecular first-order law. The rates of reaction are expressible by the Arrhenius equations $k = 10^{13.09} \exp(-38,110/RT)$ and $k = 10^{12.77} \exp(-36,090/RT)$ for the chloroacetate and the dichloroacetate, respectively. An attempt has been made to relate the results to the electronic effects involved in the reaction.

MANY carboxylic esters have been pyrolysed in recent years with the formation of olefins and carboxylic acids.^{1,2} The mechanism of these reactions has been interpreted in terms of electronic theory³ and a six-centred transition state (cf. I) has been accepted. Discussions of this mechanism have centred round the relative importance of the nature

¹ Trotman-Dickenson, "Gas Kinetics," Butterworths Scientific Publins., London, 1955, p. 129.

² Emovon and Maccoll, *J.*, 1962, 335.

³ Maccoll, *J.*, 1958, 3398.

of the breaking C-O and the forming O-H bonds and the stability of the olefins formed. DePuy and his co-workers⁴ have suggested that there is no appreciable formal charge separation in the transition state, which they describe in terms of the simultaneous breaking of C-O and C-H bonds and the development of double-bond character in the C-C bond. They⁵ also observed that ester pyrolysis is insensitive to inductive and resonance effects. Smith and his co-workers,⁶ in a systematic study of the factors determining the stability of esters, concluded that the mechanism can be best described in terms of the character of the C-O bond and the withdrawal of electrons from hydrogen in the β -position, the former effect being principally responsible for the stability of carboxylic esters.

The object of the present work is to provide further evidence of the inductive effect on the rate of reaction of esters and also to examine the effect, in the absence of any strongly influencing group in the alkyl portion, of the forming O-H bond on the reaction rate constant. *t*-Butyl mono- and di-chloroacetate, which produce only one olefin, have been chosen, so that the effect of the stability of the olefinic product on the rate of decomposition remains constant. It had been found that esters of strong carboxylic acids decomposed at low temperatures,⁷ but no quantitative effect of strong acids on the rates had been investigated. The present work could not be extended to the trichloroacetate because of the large yield of hydrogen chloride produced from the trichloroacetic acid on pyrolysis.

Experimental.—Preparation. The esters were prepared by refluxing *t*-butyl alcohol with the appropriate acid in benzene under a Dean-Stark apparatus.⁸ The purity of the esters obtained by fractionation through an efficient column was checked by analysis and vapour-phase chromatography.

t-Butyl chloroacetate had b. p. 67—68°/29—30 mm., n_D^{21} 1.4229 (lit.,⁹ b. p. 58—59°/18 mm., n_D^{25} 1.4207) (Found: C, 48.1; H, 7.8. Calc. for $C_6H_{11}ClO_2$: C, 47.85; H, 7.4%). *t*-Butyl dichloroacetate had b. p. 78.5—79°/30 mm., n_D^{24} 1.4323 (Found: C, 39.7; H, 5.7. $C_6H_{10}Cl_2O_2$ requires C, 38.9; H, 5.45%). Commercial (B.D.H.) cyclohexene was purified² and distilled in an atmosphere of nitrogen and the fraction boiling at 82.6°/754 mm. (n_D^{24} 1.4455) was collected (lit.,² b. p. 83°, n_D^{25} 1.4451).

Pyrolyses of *t*-butyl esters were carried out in a static system with an aged vessel seasoned with the products of decomposition of allyl bromide and the esters. The progress of the reaction was followed by pressure measurements at a glass diaphragm gauge. The products of decomposition were analysed by vapour-phase chromatography and by titration of acid with sodium hydroxide. The products were shown to be predominantly isobutene and the respective acid. At higher temperatures, however, the acids formed appeared to be unstable, which probably accounted for traces of hydrocarbons in the chromatograms for these temperatures.

Results and Discussion.—The reactions were observed to be homogeneous, unimolecular, and of the first order. An increase in the surface: volume ratio did not sensibly alter the rates of decomposition of the esters (Table 1).

TABLE 1.

Bu ^t ester	Temp.	No. of runs	10 ⁴ <i>k</i> (packed) (sec. ⁻¹)	No. of runs	10 ⁴ <i>k</i> (unpacked) (sec. ⁻¹)
Chloroacetate	235.5°	3	5.51	6	5.39
Dichloroacetate	225.7°	8	9.33	4	9.32

The absence of a chain reaction was verified by carrying out some runs in the presence of cyclohexene as inhibitor.² The mean values of the rate constants in the presence and in the absence of cyclohexene showed no significant inhibition (Table 2).

⁴ DePuy, King, and Froemsdorf, *Tetrahedron*, 1959, **7**, 123.

⁵ DePuy, Bishop, and Geoders, *J. Amer. Chem. Soc.*, 1961, **83**, 2151.

⁶ Smith, Bagley, and Taylor, *J. Amer. Chem. Soc.*, 1961, **83**, 3647.

⁷ Smith and Wetzel, *J. Amer. Chem. Soc.*, 1951, **73**, 875.

⁸ Liston and Dehn, *J. Amer. Chem. Soc.*, 1938, **60**, 1264.

⁹ Johnston, Belew, Chima, and Hemt, *J. Amer. Chem. Soc.*, 1953, **75**, 4998.

TABLE 2.
Effects of cyclohexene on rates.

Temp.	Monochloroacetate				Temp.	Dichloroacetate			
	p_0 (mm.)	p_c (mm.)	p_0/p_c	10^4k (sec. ⁻¹)		p_0 (mm.)	p_c (mm.)	p_0/p_c	10^4k (sec. ⁻¹)
258.7°	166.2	186.0	0.895	24.77	231.5°	214.0	133.0	1.61	14.2
„	181.5	—	—	25.17	„	135.0	—	—	14.4
235.0	197.5	143.0	1.38	5.50	245.7	168.3	117.0	1.44	36.83
„	166.7	—	—	5.48	„	109.0	—	—	36.81

p_0 is the initial pressure of the ester, and p_c the pressure of cyclohexene.

The reactions were studied in the initial pressure range of 10.0—30.0 cm. and the rate constants were found to be independent of the initial pressure (Table 3).

TABLE 3.
Effect of initial pressure on the rate constants.

Decomn. of $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Bu}^t$						
Initial press., p_0 (mm.)	115.0	204.5	123.3	181.5	140.6	
10^4k (sec. ⁻¹)	25.09	25.19	25.28	25.19	25.00	
Decomn. of $\text{CHCl}_2\cdot\text{CO}_2\text{Bu}^t$						
Initial press., p_0 (mm.)	120.6	221.0	280.0	128.0	127.3	
10^4k (sec. ⁻¹)	9.54	8.74	9.51	8.36	9.50	

The mean values of the ratio $t_{0.5}/t_{0.25}$ for the mono- and the di-chloroacetate were 2.47 at 266.5° and 2.50 at 231.5°, respectively. These agree, within experimental error, with the theoretical value of 2.42 for a first-order reaction.

The rate constants were obtained graphically from the relation $k = (2.303/t) \log p_0/(2p_0 - p_t)$, where p_t is the total pressure at time t . This relation is based on the stoichiometry $\text{R}\cdot\text{CO}_2\text{C}_n\text{H}_{2n+1} \rightarrow \text{R}\cdot\text{CO}_2\text{H} + \text{C}_n\text{H}_{2n}$, which is supported by the ratio of the final (p_∞) to initial (p_0) pressures (Table 4). Also a reasonable agreement has been obtained between the calculated extent of decomposition from pressure measurements

TABLE 4.
Ratio of final to initial pressures.

Temp.	Bu ^t chloroacetate			Bu ^t dichloroacetate		
	p_0 (mm.)	235.5°	258.7°	266.5°	214.1°	225.7°
p_∞/p_0	76.0	189.6	159.3	123.4	186.6	103.0
p_∞/p_t	1.96	2.00	1.98	2.06	1.96	2.00

TABLE 5.
Stoichiometry.

Decomp. (%)	Monochloroacetate				Dichloroacetate			
	(press.)	(anal.)	(press.)	(anal.)	(press.)	(anal.)	(press.)	(anal.)
Decomp. (%) (press.)	15.4	23.6	40.3	70.2	20.1	32.3	58.2	80.3
Decomp. (%) (anal.)	16.2	25.0	38.9	68.7	21.2	33.0	57.6	77.8

TABLE 6.
Pyrolysis in an unpacked vessel.

(a) Chloroacetate						
Temp.	266.5°	258.7°	248.0°	235.5°	226.0°	216.0°
10^4k (sec. ⁻¹)	45.59	25.11	13.14	5.39	2.54	1.15
No. of runs	10	7	10	6	5	5
(b) Dichloroacetate						
Temp.	246.8°	237.0°	231.5°	225.7°	214.1°	
10^4k (sec. ⁻¹)	39.81	19.95	14.13	9.33	3.85	
No. of runs	7	8	7	8	7	

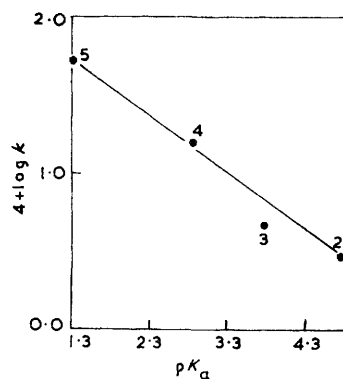
and that from direct titration of the chloroacetic acids produced (Table 5). The discrepancy in the results in Table 5 is attributed to slight hydrolysis and gradual evolution of hydrogen chloride by decomposition of the acid.

The temperature dependence of the first-order rate constants is given in Table 6.

The entropies of activation for the pyrolyses of esters with hydrogen in the β -position have negative values and have been quoted¹⁰ in support of the cyclic nature of the transition

Relationship of rate of pyrolysis of *t*-butyl ester with the acid dissociation of the acid.

1, Propionic. 2, Acetic. 3, Formic.
4, Chloroacetic. 5, Dichloroacetic.



state. For normal reactions, however, little significance attaches to these results (Table 7) since only when a large deviation of the A factor from 10^{13} is observed can one justifiably look to molecular structure for explanations.

TABLE 7.

Bu ^t ester	E (kcal. mole ⁻¹)	$\log A$ (sec. ⁻¹)	ΔS^* (cal. mole ⁻¹ deg. ⁻¹)	Rel. rate (250°)
Formate ¹¹	34.60	11.11	10.81	1.62
Acetate ²	40.02	13.15	0.83	1.00
Propionate ¹²	39.20	12.80	3.07	0.98
Chloroacetate	38.11	13.09	1.75	5.50
Dichloroacetate	36.09	12.77	3.21	18.60

Smith and his co-workers⁶ have concluded from pyrolyses of substituted benzoates that substituents which reduce electron density at the carbonyl position increase the rate of reaction. Blades¹³ also suggested that a similar effect operates in ester pyrolysis and in acid dissociations. Replacement of a hydrogen atom in acetic acid by chlorine increases the acid strength while a methyl substituent decreases it:

Acid	Formic	Acetic	Propionic	Chloroacetic	Dichloroacetic
pK_a	3.75	4.75	4.85	2.85	1.3

These changes result from the inductive effects of substituents. The rates of decomposition of the esters investigated have been observed to follow the same sequence as acid strength (Table 7), as shown in the Figure, but with much reduced relative values.

In the systems studied, the chlorine atom exerts a strong inductive electron pull on the ester group and thereby facilitates the transfer of the lone pair of electrons from the ether-oxygen into the carbonyl-carbon-oxygen single bond. An incipient double bond develops at this position, weakening the alkyl-oxygen bond. At the same time, the basicity of the carbonyl-oxygen atom, which acquires a formal negative charge by the mesomeric electron shift, is reduced by the chlorine atom. This electron distribution leaves the ether-oxygen with a formal positive charge which is subsequently relayed by

¹⁰ Blades, *Canad. J. Chem.*, 1954, **32**, 366.

¹¹ Gordon, Price, and Trotman-Dickenson, *J.*, 1957, 2813.

¹² Warrick and Fugassi, *J. Phys. Chem.*, 1948, **52**, 1314.

¹³ Blades, *Canad. J. Chem.*, 1960, **38**, 1412.

the inductive mechanism to the β -hydrogen atom of the t-butyl group. This state is stabilised by interaction of the C-Cl dipole, leading to a high rate of reaction.

Decreasing the basicity of the carbonyl-oxygen atom would decrease the rate of formation of the O-H bond between the carbonyl-oxygen and the acidic β -hydrogen atom of the t-butyl group. This should reduce the rate of decomposition if the forming O-H bond primarily determines the rate. This, however, is contrary to observation (Table 7) and hence it may be concluded that the forming O-H bond has little effect on the rate of decomposition of these esters.

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