The Mechanism of the Gas-phase Pyrolysis of Esters. Part 7.[1] The Effects of Substituents at the Acyl Carbon

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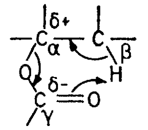
Some t-butyl esters of substituted acetates ($RCH_2CO_2Bu^t$) have been prepared and pyrolysed at temperatures between 620 and 519 K. The rate data give an approximate correlation with σ_I values (ρ = *ca.* 1.4 at 600 K), deviations being most probably due to steric acceleration of elimination when the substituent at the acyl carbon is bulky. This is also indicated by the fact that isopropyl pivalate and t-butyl pivalate each pyrolyse more rapidly than their corresponding acetates whereas on electronic grounds alone the reverse reactivity order should obtain. An alternative explanation of these anomalies is that hyperconjugation leads to increased nucleophilicity of the carbonyl oxygen, and this may in particular account for the high reactivity of t-butyl trimethylsilylacetate.

IN pyrolysis of esters, electron-withdrawing substituents at the γ or acyl carbon (1) increase the rate of elimination



(1)

so that a reactivity series is: acetates < phenylacetates < benzoates < *N*-phenylcarbamates < phenyl carbonates.[2] Likewise substituents in the aryl ring attached to the acyl carbon give good Hammett correlations with σ^0 or σ^n values, the ρ factors being positive.[1,3,4] Accordingly it could be anticipated that esters of the type $R{\cdot}CH_2CO_2R'$ might thermally eliminate with rates which correlated with σ_I values for the substituent R, and therefore might provide a gas-phase method of determining these parameters. A range of these esters have therefore been prepared and pyrolysed,

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[1] Part 6, H. B. Amin and R. Taylor, *J.C.S. Perkin II*, **1978**, 1095.

[2] R. Taylor, *J.C.S. Perkin II*, **1975**, 1095.

[3] G. G. Smith, D. A. K. Jones, and D. F. Brown, *J. Org. Chem.*, 1963, **28**, 403; G. G. Smith and D. A. K. Jones, *ibid.*, p. 3896; G. G. Smith, D. A. K. Jones, and R. Taylor, *ibid.*, p. 3547.

[4] H. B. Amin and R. Taylor, *J.C.S. Perkin II*, **1975**, 1802; R. Taylor and M. P. Thorne, *ibid.*, **1976**, 799.

the t-butyl derivatives being chosen so that interference from secondary decomposition of the substituted acetic acid would be minimal.

TABLE 1

Pyrolysis of compounds RCO_2Bu^t

R	T/K	$10^3k/s^{-1}$	log (A/s^{-1})	$\frac{E}{\text{kcal mol}^{-1}}$	$\frac{\Delta S^{\ddagger}}{\text{cal mol}^{-1}\text{ K}^{-1}}$ [a]	Corr. coeff.	log $k_{rel.}$[a,b]
Me	c	c	13.06	39.69	−0.1	0.99975	0
Et	620.2	89.0	12.56 [d]	38.43 [d]	−2.46	0.99844	−0.0388
	604.6	47.4					
	600.8	44.3					
	587.4	19.5					
	571.3	7.39					
	557.9	3.22					
	553.3	2.38					
	543.3	1.20					
Bu^tCH_2	620.2	95.0	12.72	38.80	−1.72	0.99732	−0.0180
	608.1	68.1					
	604.6	52.9					
	587.4	18.8					
	571.2	7.34					
	557.9	3.24					
$MeOCH_2$	587.4	33.0	13.49	40.20	1.80	0.99979	0.2438
	571.3	13.6					
	557.9	5.49					
	543.3	2.06					
	527.8	0.696					
$BrCH_2$	587.4	72.2	12.64	36.96	−2.10	0.99919	0.5801
	571.3	34.0					
	557.9	15.55					
	543.3	5.94					
	527.7	2.29					
	518.8	1.11					
$ClCH_2$	587.4	71.0	12.49 [e]	36.58 [e]	−2.78	0.99921	0.5633
	571.3	32.8					
	557.9	15.35					
	543.3	6.04					
	527.7	2.09					
Bu^t	604.6	63.7	13.02	39.51	−0.35	0.99985	0.0980
	587.4	25.2					
	571.3	9.43					
	557.9	4.27					
	553.3	3.19					
	543.3	1.56					
$SiMe_3$	608.1	124	14.63	43.28	7.0	0.99969	0.258
	604.6	91.7					
	600.8	73.9					
	587.4	31.9					
	559.4	5.14					
	557.9	5.10					
	543.3	1.81					
	529.7	0.600					
	527.7	0.473					
	518.8	0.235					

[a] At 600 K. [b] Relative to the rate of pyrolysis of t-butyl acetate. [c] Kinetic data given in Part 5: H. B. Amin and R. Taylor, *J.C.S. Perkin II*, 1978, 1090. [d] Literature values (E. Werrick and P. Fugassi, *J. Phys. Chem.*, 1948, **52**, 1314) are 12.79 s^{-1} and 39.16 kcal mol^{-1}. [e] Literature values [17] (determined over a smaller temperature range) were 13.09 s^{-1} and 38.1 kcal mol^{-1}. The rate coefficients are in excellent agreement over the common temperature range studied.

In an earlier part of this series, we showed that interaction between bulky substituents at the α- and β-carbon atoms produces acceleration of the elimination rate,[5] and this explained the anomalous activation by β-alkyl substituents. The acyl group is, of course, an α-substituent so that one might expect that bulk in the former might also produce steric acceleration. Some indication that this is so comes from the fact that ethyl pivalate pyrolyses *ca.* 1.1 times faster than ethyl acetate,[6] cyclohexyl pivalate pyrolyses 1.4 times faster than cyclohexyl acetate,[7] and for the *cis*- and *trans*-2-chloro-derivatives these factors are 1.46 and 1.64—1.67, respectively.[7] Isopropyl pivalate was also reported to pyrolyse 30—45% faster than isopropyl acetate[8] but the kinetic data were anomalous in that the difference *increased* with increasing temperature. We have, therefore, examined the reactivity towards thermal elimination of t-butyl pivalate since steric acceleration could be expected to be most pronounced for this, and also re-examined the pyrolysis of isopropyl pivalate *vs.* isopropyl acetate to ascertain the cause of the anomaly noted above.

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[5] S. de Burgh Norfolk and R. Taylor, *J.C.S. Perkin II*, 1976, 280.

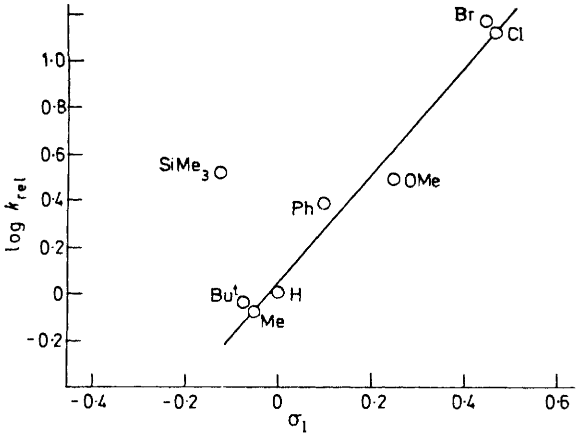
[6] J. T. D. Cross and V. R. Stimson, *Australian J. Chem.*, 1967, **0**, 177.

[7] A. Tinkelberg, E. C. Kooyman, and R. Louw, *Rec. Trav. Chim.*, 1972, **91**, 3.

[8] B. S. Lennon and V. R. Stimson, *Australian J. Chem.*, 1968, **21**, 1659.

RESULTS AND DISCUSSION

The kinetic data are given in Tables 1 and 2 and those for t-butyl phenylacetate are given in ref. 2. The data in Table 1 (and ref. 2) show that, in general, electron withdrawal speeds up the elimination rate and electron supply decreases it, so that an approximate correlation of log $k_{rel.}$ *vs.* σ_I constants [9] is obtained (Figure) with $\rho = ca.$ 1.4 at 600 K. (Some preliminary data were also obtained with t-butyl cyanoacetate, but the secondary decomposition of cyanoacetic acid was sufficiently fast as to prevent accurate determination of the first-order rate coefficients for the primary elimination. However, it was clear that this was faster than for any other ester studied, as expected from the σ_I value for CN or 0.58.)



Correlation of pyrolysis rates for esters $RCH_2CO_2Bu^t$ *vs.* σ_I constants for R

TABLE 2

Pyrolysis of compounds RCO_2Pr^i

R	T/K	$10^3\ k$/s^{-1}	log (A/s^{-1})	E / kcal mol^{-1}	$\Delta S^{\ddagger\ a}$ / cal mol^{-1} K^{-1}	Corr. coeff.	log $k_{rel.}$ [a,b]
Me	668.1	17.9	13.21 [c]	45.69 [c]	0.52	0.99991	0
	650.0	7.18					
	629.2	2.17					
	609.2	0.65					
Bu^t	667.3	22.3	13.03 [d]	44.83 [d]	−0.31	0.99979	0.137
	652.6	10.5					
	620.2	1.80					
	608.9	0.85					

[a] At 600 K. [b] Relative to the rate of pyrolysis of isopropyl pivalate. [c,d] The literature values [8] for isopropyl pivalate (12.88 s^{-1} and 44.78 kcal mol^{-1}) are in excellent agreement with those obtained here. By contrast the literature values [8] for isopropyl acetate (12.09 s^{-1} and 42.9 kcal mol^{-1}) are much too low and must refer to a reaction with a surface-catalysed component. This caused the anomalously temperature-dependent pivalate : acetate reactivity ratio given in the literature.

It is evident that the correlation in the Figure is poor in contrast to those obtained when these substituents are removed from the reaction site by a benzene ring and this suggests that some other interaction such as steric acceleration is responsible. This view is supported by the relative reactivities of t-butyl bromoacetate to t-butyl chloroacetate, and of t-butyl t-butylacetate to t-butyl propionate; the bulky t-butyl phenylacetate also appears to be eliminating faster than expected. The most dramatic deviation is, however, obtained with the trimethylsilyl acetate which is also the bulkiest of the esters examined.

We also find (Table 1) that t-butyl pivalate is more reactive than t-butyl acetate ($k_{rel.}$ = 1.25 at 600 K) and (Table 2) that isopropyl pivalate is more reactive than isopropyl acetate ($k_{rel.}$ = 1.37 at 600 K). [In contrast to the literature report this latter factor decreases with increasing temperature, *i.e.* the activation energy is lower for the most reactive compound. The literature activation energy for isopropyl acetate was anomalously low (considerably lower than that obtained in any other study [10]) and appears to have been affected by surface-catalysed elimination even though the usual criteria were said to indicate the absence of this.[8]] Since the t-butyl group is more electron-releasing than methyl, a reverse reactivity order could be expected so it appears that the observed order does not have an electronic organ and steric acceleration is the obvious explanation. This being so, the acceleration should be greater in the tertiary ester than in the secondary one. This is not observed which may reflect the fact that the transition state for elimination from tertiary esters is more polar than that for elimination from secondary esters; [2,11] the greater (rate-retarding) electronic effect of t-butyl *vs.* methyl will be more pronounced in the tertiary esters and will more effectively oppose the reverse reactivity sequence arising from steric acceleration.

Since propionate esters ($CH_3CH_2CO_2R$) are less reactive than acetates whereas pivalates [$(CH_3)_3CO_2R$] are more reactive than acetates, it may be anticipated that 2-methyl propionates which have intermediate electronic and steric requirements, will have virtually identical reactivity to acetates.

Although we have attributed the marked reactivity of t-butyl trimethylsilylacetate to steric acceleration, an alternative explanation cannot be ruled out. This involves C–Si hyperconjugation, known to be very strong,[12] and which releases electrons to the carbonyl oxygen (2) thereby facilitating nucleophilic attack on the

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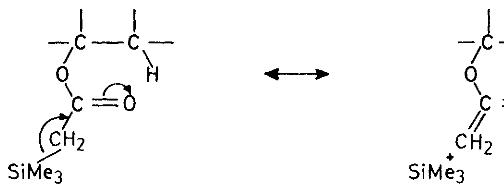
[9] R. W. Taft, *J. Phys. Chem.*, 1960, **64**, 1805.

[10] G. G. Smith and F. W. Kelly, *Progr. Phys. Org. Chem.*, 1971, **9**, 150.

[11] H. B. Amin and R. Taylor, *J.C.S. Perkin II*, 1975, 1802; 1979, in the press.

[12] C. Eaborn, T. A. Emokpae, V. I. Sidorov, and R. Taylor, *J.C.S. Perkin II*, 1974, 1454.

β-hydrogen. Such a process could account for the higher reactivity of the pivalates relative to the acetates since C–C hyperconjugation is more important than C–H hyperconjugation.[13] This argument also predicts (as does steric acceleration) that acetates should be more reactive than formates but, unfortunately, the literature data for formates appears confused, since ethyl, isopropyl, and t-butyl formates can be more or less reactive than the corresponding acetates depending upon the temperature [14,15] and we believe that some, if not all, of the formate data refers to a partly surface-catalysed elimination which shows up for example in the anomalously low activation energy for pyrolysis of t-butyl formate (which was also studied in an unseasoned reactor). Against the hyperconjugation explanation may be set the fact that this should show up as a reduced activation energy whereas this is not observed.



(2)

EXPERIMENTAL

t-Butyl acetate and t-butyl phenylacetate were available from previous studies.[11] The following esters were prepared by standard methods: t-butyl propionate (b.p. 118 °C at 760 mmHg, n_{D}^{20} 1.393 2, lit.,[16] 121 °C at 760 mmHg, n_{D}^{20} 1.393 2); t-butyl chloroacetate (b.p. 86 °C at 60 mmHg. n_{D}^{20} 1.423 6, lit.,[17] 67—68 °C at 29—30 mmHg, n_{D}^{21} 1.422 9); t-butyl bromoacetate (b.p. 88 °C at 60 mmHg, n_{D}^{20} 1.442 2, lit.,[18] 62—63 °C at 14 mmHg); t-butyl methoxyacetate (b.p. 76 °C at 60 mmHg, n_{D}^{20} 1.493 9, lit.,[16] b.p. 62—64 °C at 22 mmHg, n_{D}^{20} 1.498 7); t-butyl pivalate (b.p. 132 °C at 760 mmHg, n_{D}^{20} 1.391 8, lit.,[19] 135 °C at 760 mmHg, n_{D}^{20} 1.392 0); isopropyl pivalate (b.p. 123 °C at 760 mmHg, n_{D}^{20} 1.390 0, lit.,[8] b.p. 121 °C at 670 mmHg, n_{D}^{17} 1.390 7); and *t-butyl t-butylacetate* (5 g, 29%), b.p. 92 °C at 60 mmHg, n_{D}^{20} 1.406 3 (Found: C, 69.6; H, 5.8. $C_{10}H_{20}O_2$ requires C, 69.7; H, 5.85%).

t-Butyl trimethylsilylacetate. This compound was prepared according to the general principles given in refs. 20 and 21. Preparation of the required compound was claimed in the latter reference but no properties were recorded. Triphenylmethane (18 g, 0.074 mol) was dissolved in tetrahydrofuran (100 ml) and a solution of n-butyllithium (46 ml of a 1.5M-solution in hexane) was added and the mixture heated under reflux to form the triphenylmethyl carbanion; in the absence of heating this does not form to a significant extent. t-Butyl acetate (8.6 g, 0.074 mol) was added at −78 °C and the mixture allowed to warm to *ca.* −50 °C when the colour of the solution disappears indicating reformation of triphenylmethane. Trimethylsilyl chloride (excess) was then added, the mixture being allowed to attain room temperature. Work-up followed by fractional distillation gave *t-butyl trimethylsilylacetate* (4 g, 29%), b.p. 90 °C at 60 mmHg, n_{D}^{20} 1.416 2 (Found: C, 57.0; H, 10.7. $C_9H_{20}O_2S$ requires C, 57.1; H, 10.6%).

Kinetics.—The general procedure has been described.[22] Excellent first-order kinetics (linear to beyond 95% of reaction) were obtained for t-butyl acetate, propionate, t-butylacetate, and pivalate, and for isopropyl acetate and pivalate. For esters with electron-withdrawing substituents at the acyl position, secondary decomposition of the substituted acetic acid by-product was significant especially at the highest temperatures (since this decomposition has an activation energy which is higher than for the primary elimination). For these esters significant curvature of the first-order kinetic plots was evident after *ca.* 75% of reaction, so that the rate coefficients were determined over the first portion of reaction only. For t-butyl trimethylsilylacetate excellent first-order plots were obtained at the highest temperatures but at lower temperatures some curvature was evident which is believed to be associated with the low volatility of the ester causing it to take an appreciable time to attain thermal equilibrium. The rate coefficients were, therefore, determined over the last 80% of reaction for these runs; the stoicheiometry for decomposition of this ester was 2.0 ± 0.03 throughout the temperature range.

[8/132 *Received*, 26*th January*, 1978]

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[13] E. Glyde and R. Taylor, *J.C.S. Perkin II*, 1977, 678.

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[15] E. Gordon, S. J. W. Price, and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1957, 2813.

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[17] E. V. Emovon, *J. Chem. Soc.*, 1963, 1246.

[18] 'Dictionary of Organic Compounds,' Eyre and Spottiswoode, London, 1965.

[19] N. C. Cook and W. C. Percival, *J. Amer. Chem. Soc.*, 1949, **71**, 4141.

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