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GAS–PHASE PYROLYTIC REACTIONS. PART 3.[1]

HAMMETT ρ CONSTANTS OF GAS–PHASE ELIMINATIONS OF ALKYL ARYLCARBOXYLATE AND ETHANOATE ESTERS AND THEIR CORRELATION WITH SUBSTRATE MOLECULAR FRAMEWORK

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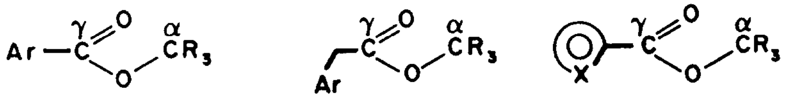
Abstract: The kinetics of the gas–phase thermal elimination of seven tert–butyl (hetero)arylcarboxylate esters (GCO_2Bu^t) were measured over a temperature range ≐ 50 K; the groups were the phenyl, 3– and 4–pyridyl, 2– and 3–furyl, and 2– and 3–thienyl moieties. The reactions were homogeneous and unimolecular with log $\underline{A}/s^{-1}$ scaling 12.45 ± 0.44, and with an entropy of activation uniformly negative and small. The kinetics obeyed a first–order rate equation, and at 600 K the rate coefficients ($10^3 k/s^{-1}$) of the esters, in the order given above, were: 54.1, 85.3, 120.5, 76.9, 43.2, 86.3 and 46.1, respectively. Hammett correlation of the present kinetic data with the literature σ°–values of the given substituents gave a reaction ρ constant compatible with the ethanoate molecular frame rather than with the carboxylate structure. The physical constants of five new t–butyl heteroarylcarboxylate esters are also described.

Introduction

From work on the pyrolysis of a series of ethyl, isopropyl, and tert–butyl benzoate and phenylethanoate esters,[2-6] it was argued that the reaction pathway for these gas–phase eliminations involves a polar transition state with concomitant and commensurate positive and negative charges, respectively, at the α– and γ– carbon atoms of the ester (Figure 1). The argument was based on data from both relative rate measurements and Hammett ρ/σ correlations. Furthermore, the spread of rates and ρ–values, together with sign and relative magnitude of ρ–parameters, were used as indicators of the degree of polarity of the transition state, and of the sign and magnitude of charge developed at the reference carbon centres. The alkyl esters associated with the highest degree of transition state polarity were those of the t–butyl group.



(1) (2) (3)

Figure 1. Alkyl arylcarboxylate (1), arylethanoate (2) and heteroarylcarboxylate (3) ester frames.

The reaction ρ constants at 600 K of the ethyl, isopropyl, and t–butyl carboxylate esters substituted at the γ–carbon centre were found to be 0.26, 0.335 and 0.58, respectively; the ρ–value of the t–butyl ethanoate ester was 0.39. The best Hammett correlations were those based on σ^0 and σ^n substituent constants.[7,8] These findings were considered an indication of the low susceptibility of these molecular structures to transmission of electronic substituent effects through resonance interactions. It was, however, argued that resonance effects were not wholly unfavourable to arylcarboxylate ester (1) eliminations.[6] The arylethanoate frame (2), on the other hand, has an extra CH_2 unit fitted between the ester group and the aryl moiety. Such insertions were reported to have further reduced resonance interactions.[9,10] It is of interest to note that the heteroatoms (x) of the heteroaryl groups of the carboxylate esters (3), if viewed as substituents in their own right[11] rather than as complementary units in the heterocyclic rings, would be part of molecular frames closer in structure to the arylethanoate system than to arylcarboxylates.

In the gas phase, pyrolysis of alkyl (hetero)arylcarboxylate esters invariably produced the corresponding carboxylic acids and the alkene analogues of the alkyl groups. Product analysis confirmed that the present reaction was no exception. In this study particular care was taken to ensure that the kinetic runs were free of reactor–surface effects.

Results and Discussion

Table 1 summarizes the first–order rate coefficients of the gas–phase eliminative reactions of the tert–butyl benzoate and the corresponding tert–butyl carboxylate esters substituted at the 3– and 4–positions of pyridine and the 2– and 3–positions of furan and thiophene. The rate coefficients of

Table 1. Rate Coefficients ($10^3k/s^{-1}$) for (Hetero)aryl GCO_2CMe_3 Ester Pyrolysis.

G =	Phenyl		3–Pyridyl		4–Pyridyl		2–Furyl	
	T/K	k	T/K	k	T/K	k	T/K	k
	559	4·68	551	4·96	549	6·57	560	8·88
	563	6·76	555	6·28	553	7·86	573	17·41
	570	10·88	557	7·50	559	9·61	576	20·79
	572	10·96	559	8·14	561	13·70	578	23·22
	576	13·70	569	16·10	577	36·30	582	28·90
	578	15·06	578	26·00	586	58·90	584	33·80
	587	24·83	586	41·70	588	70·79	590	46·45
	596	45·08	593	59·20	594	85·10	592	49·43
	597	45·60	600	86·70	598	107·2	596	64·41
	608	77·09	606	95·90	602	125·9	599	75·85
	612	96·82	608	113·2			602	82·41
	617	127·3					606	91·83
							611	129·8

G =	3–Furyl		2–Thienyl		3–Thienyl	
	T/K	k	T/K	k	T/K	k
	561	5·08	550	5·36	560	4·84
	568	7·68	553	6·06	566	7·80
	575	10·76	557	7·91	572	10·90
	580	15·77	560	9·30	579	13·58
	582	17·29	568	15·06	584	20·94
	585	20·09	570	18·36	589	26·47
	587	21·67	574	22·33	594	35·39
	593	29·92	582	35·97	601	47·97
	603	54·07	586	37·41	607	60·95
	604	56·62	592	58·47	609	75·68
	610	67·76	598	84·72		
			600	86·69		

Table 2. Arrhenius Parameters and Rate Data at 600 K for Pyrolysis of (Hetero)aryl GCO_2CMe_3 Esters.

G	log A/s^{-1}	E_a/kJ mol^{-1}	$\Delta S^{\ddagger}$/J mol^{-1} K^{-1}	Corr. coef.	10^3k/s^{-1}	log k_{rel}.
Phenyl	12·64	159·58	−8·91	0·999	54·1	
3–Pyridyl	12·34	153·97	−14·5	0·998	85·3	0·198
4–Pyridyl	12·89	158·57	−3·96	0·997	120·5	0·348
2–Furyl	12·12	151·96	−18·7	0·998	76·9	0·153
3–Furyl	12·01	153·47	−21·0	0·999	43·2	−0·098
2–Thienyl	12.34	153.80	−14·6	0·998	86·3	0·203
3–Thienyl	12·01	153·13	−21·0	0·998	46·1	−0·069

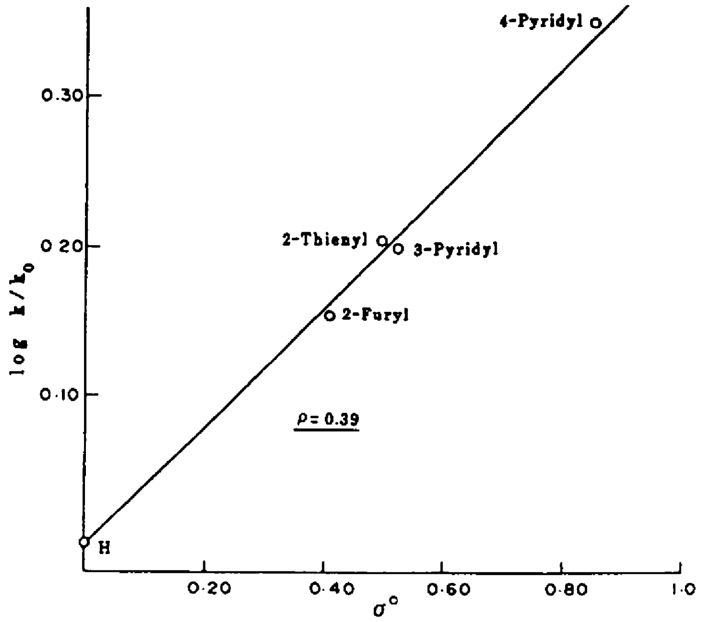


Figure 2. Log k/k$_0$ vs σ° substituent constants for gas-phase elimination of t-butyl heteroarylcarboxylate esters .

individual esters were followed over the 50 K temperature range deemed necessary for reliable kinetic analysis. Table 2 presents the relative rates computed at 600 K, and the relevant Arrhenius parameters derived for the six heterocyclic groups. The Arrhenius energies and entropies of activation agree with the structural requirements of the transition state proposed for ester elimination pathways,[12] and, together with the spread of the rate coefficients in individual kinetic runs, seem to suggest the absence of surface–catalysis and, hence, the reliability of kinetic measurements.

The log k_{rel} values obtained in this study for the pyrolysis of t–butyl heteroarylcarboxylate esters are plotted (Figure 2) against the σ^0–values of the heterocyclic groups. These substituent constants are abstracted from the data compiled by Exner,[13] and the σ^0–values are based on the work of Blanch[1] and of Otsuji et al.[15] on the hydrolysis of substituted carboxylate esters and ionization of substituted phenylethanoic acids. The Hammett ρ–value calculated from the plot for the gas phase elimination of the t–butyl heteroarylcarboxylate ester is 0.39 (600 K). This value is notably different from ρ obtained[5] for the corresponding t–butyl arylcarboxylate ester (0.58 at 600 K), but is in complete agreement with the ρ–value of the t–butyl arylethanoate ester system.[6] Implicit in these findings are the following observations: (a) substituent σ^0 constants give reliable and acceptable Hammett correlations for the gas–phase eliminations of alkyl (hetero)arylcarboxylate and ethanoate esters; (b) the Hammett σ/ρ parameters seem to reflect the structural resemblance of the heteroarylcarboxylate frame (3) to the arylethanoate carbon skeleton (2) insofar as the former system incorporates at least one carbon atom inserted between the ester moiety and the heteroatom functioning as an individual substituent. This structural finding is further substantiated and made use of in providing substituent σ^0 constants of heterocyclic groups.[16]

Experimental

Kinetic Studies.— The flow system used for measuring reaction rates is, and the techniques of kinetic data analysis have been described.[17,18] Pyrolysis was conducted in a Eurotherm–093 pyrolysis unit, and the elimination products, together with residual reactant and reference materials, were quantitatively determined by means of g.l.c. using a Perkin Elmer Sigma 115 gas chromatograph. Rates were measured over a temperature range of 50 K or more between about 550 – 615 K, and care was taken to ensure absence of adverse reactor–surface effects. For each ester and at each reaction temperature, the rate coefficient represents an average of four kinetic runs whose rates remain within a ± 2% limit.

Product Analysis.— The products of the elimination reactions were analyzed using a tubular glass reactor packed with helices and heated to temperatures compatible with those established from kinetic investigations.[19] Reaction mixtures were eluted using a stream of nitrogen gas, and were collected in receivers contained in a dry–ice/acetone bath. The elimination products were confirmed as being the corresponding carboxylic acids expected from pyrolysis of the esters. Characterization of the acids produced was based on their i.r. and n.m.r. data as follows: benzoic acid, ν_{max} 1720 (CO), 2980 (OH), δ ($CDCl_3$) 7.2 (5 H, m, Ph), 2.2 (1 H, s, OH); thiophene–2–carboxylic acid, ν_{max} 1705 (CO), 2920 (OH), δ ($CDCl_3$) 6.88 (1 H, t, H–4), 7.4 (1 H, d, H–3), 7.6 (1 H, d, H–5), 2.2 (1 H, s, OH); thiophene–3–carboxylic acid, ν_{max} 1710 (CO), 2980 (OH), δ ($CDCl_3$) 7.0 (1 H, d, H–4), 7.4 (1 H, d, H–5), 7.6 (1 H, s, H–2) 2.2 (1 H, s, OH); furan–2– carboxylic acid, ν_{max} 1710 (CO), 2980 (OH), δ ($CDCl_3$) 6.3 (1 H, t, H–4), 6.8 (1 H, d, H–3), 7.2 (1 H, d, H–5), 2.0 (1 H, s, OH); furan–3–carboxylic acid, ν_{max} 1710 (CO), 2980 (OH), δ ($CDCl_3$) 7.0 (1 H, d, H–4), 7.4 (1 H, d, H–5), 7.6 (1 H, s, H–2), 2.0 (1 H, s, OH); pyridine–3–carboxylic acid, ν_{max} 1720 (CO), 2980 (OH), δ ($CDCl_3$) 6.4 (1 H, t, H–5), 7.2 (1H, d, H–4), 7.4 (1 H, d, H–6), 8.2 (1 H, s, H–2), 2.2 (1 H, s, OH); pyridine–4–carboxylic acid, ν_{max} 1720 (CO), 2920 (OH), δ ($CDCl_3$), 6.8 (2 H, d, H–3, 5), 7.5 (2 H, d, H–2, 6), 2.2 (1 H, s, OH).

Materials.— The acid chlorides required in the synthesis were prepared from the corresponding carboxylic acids obtained commercially, and following literature procedures.[20-23] The heterocyclic t–butyl esters were prepared by heating the acid chlorides with sodium t–butoxide under reflux during 2–3 hrs; tert–butyl benzoate was synthesized using t–butyl alcohol and pyridine.[5] Normal work–up followed by fractional distillation yielded the following esters: t–butyl 2–thienoate (60%), b.p. 58 °C at 1.0 mmHg, δ($CDCl_3$) 7.5–7.7 (1 H, d, H–5), 7.2–7.4 (1 H, d, H–3), 6.8–7.0 (1 H, t, H–4), 1.5 (9 H, s, CMe_3), (Found: C, 58.6; H, 6.4; S, 17.4. $C_9H_{12}O_2S$ requires C, 58.7; H, 6.5; S, 17.4%); t–butyl 3–thienoate (72%), b.p. 58 °C at 0.8 mmHg, δ ($CDCl_3$) 7.8–7.9 (1 H, m, H–2), 7.3–7.4 (1 H, m, H–5), 7.0–7.2 (1 H, m, H–4), 1.5 (9 H, s, CMe_3), (Found: C, 58.5; H, 6.5; S, 17.5%); t–butyl 2–furoate (66%), b.p. 44 °C at 1.0 mmHg, δ ($CDCl_3$) 7.4–7.5 (1 H, d, H–5), 6.9–7.0 (1 H, d,H–3), 6.3–6.5 (1 H, t, H–4), 1.5 (9 H, s, CMe_3), (Found: C, 64.1, H, 7.2. Calc. for $C_9H_{12}O_3$: C, 64.3; H, 7.1%); t–butyl 3–furoate (40%), b.p. 36 °C at 1.0 mmHg, δ ($CDCl_3$) 8.4 (1 H, s, H–2), 7.8 (1 H, d, H–5), 7.0 (1 H, d, H, H–4), 1.5 (9 H, s, CMe_3), (Found: C, 64.0; H, 7.0. $C_9H_{12}O_3$ requires C, 64.0; H, 7.1%); t–butyl nicotinate (59%), b.p. 62 °C at 1.0 mmHg, δ ($CDCl_3$) 7.6–7.8 (1 H, t, H–4), 8.6–8.8 (1 H, d, H–5), 9.2–9.4 (1 H, d, H–6), 9.6 (1 H, s, H–2), 1.6 (9 H, s, CMe$_3$), (Found: C, 67.2; N, 7.7. $C_{10}H_{13}O_2N$ requires C, 67.0; H, 7.3; N, 7.8%); t–butyl isonicotinate (28%), b.p. 62 °C at 1.0 mmHg, δ(CDCl$_3$) 9.2–9.4 (2 H, d, H–2, 6), 8.2–8.4 (2 H, d, H–3, 5), 1.6 (9 H, s, CMe$_3$), (Found: C, 67.1; H, 7.2; N, 7.8%).

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