Tetrahedron Vol. 46, No. 8, pp. 2911-2916, 1990
Printed in Great Britain

0040-4020/90 \$3.00+.00

GAS–PHASE PYROLYTIC REACTIONS. PART 4.[1]

ARRHENIUS PARAMETERS AND HAMMETT σ^o CONSTANTS IN GAS–PHASE ELIMINATIONS OF ALKYL PYRIDYL–,FURYL–, AND THIENYLCARBOXYLATE ESTERS

Nouria A. Al–Awadi*, Rasha F. Al–Bashir, and Osman M. E. ElDusouqui*

Department of Chemistry, University of Kuwait, P.O. Box 5969 Safat,

13060 Safat, Kuwait

(*Received in UK* 1 *February* 1990)

Abstract: The first–order rate coefficients ($10^5k/s^{-1}$) of the gas–phase pyrolytic reactions of seven isopropyl (hetero)arylcarboxylate esters were calculated for 600 K to be: 75.34 for benzoate, and 100.0, 70.46, 94.03, 65.58, 100.9 and 120.2 for 2–thienyl–, 3–thienyl–, 2–furyl–, 3–furyl–, 3–pyridyl– and 4–pyridylcarboxylate, respectively. The corresponding Hammett replacement σ^o substituent constants of the heterocyclic groups are: 0.53, –0.13, 0.42, –0.26, 0.55 and 0.88, respectively. The reported σ^o constants are in agreement with other gas–phase and solution data, and are amenable to rationalization in terms of normal electronic and structural effects. Further, the physical constants of four new isopropyl heteroarylcarboxylate esters are described.

Introduction

Gas–phase thermal elimination reactions of alkyl (hetero)arylcarboxylate esters are reported to proceed by pathways involving a polar transition state in which the carbon centre of the carboxylate group that is coupled to the (hetero)aryl moiety is negatively charged.[2,3] This structural feature is reflected in both rates of reactions and attendant substituent effects. Analysis based on such a kinetic and mechanistic consideration would, therefore, be expected to provide a rationale for the observed structural and electronic effects of substituents, as well as to afford a method of measuring Hammett substituent constants. It is of interest to note here that gas–phase pyrolytic reactions have the advantage of being effectively free from solvation, hydrogen–bonding and protonation effects common in solution reactions.

Replacement σ^o substituent constants of heterocyclic groups are available from solution chemistry.[4-6] However, parallel gas–phase data are lacking. The present work, therefore, seems to present the first set of gas–phase σ^o–values. The results of the work have been summarized in an earlier communication.[7]

Five– and six–membered heterocyclic substituents such as those described here reveal a subtle interplay of the electronic and structural effects of the heteroatoms and of the bonding framework of the heterocyclic ring that provides the mode by which the effects of the heteroatoms are relayed to the site being perturbed by the groups. The inductive, mesomeric, and d–orbital effects of the N, O, and S heteroatoms might be either reinforcing or counteracting; both the size of the heterocyclic ring and its nuclear position of attachment to the ester moiety are expected to contribute to the net structural and electronic effects of the heterocyclic group.[8]

Results and Discussion

Table 1 summarizes the first–order rate coefficients of the gas–phase pyrolytic reactions of isopropyl benzoate, 2– and 3–thienyl–, 2– and 3–furyl–, and 3– and 4–pyridylcarboxylate. Each rate coefficient represents an average of four kinetic runs, in agreement to within ± 2% rate spread. The kinetic profile of each ester was scanned over >50 K temperature range. The kinetic runs showed no adverse reactor–surface effects. The rates and the relative rates computed at 600 K, the relevant Arrhenius parameters, and the Hammett σ^o–values of the six heterocyclic groups are summarized in Table 2. The data on rate of reaction and Arrhenius parameters obtained here for isopropyl benzoate are in very good agreement with those reported by Taylor.[9] Table 2 also includes literature σ^o–values compiled from solution reactions.[4-6] Parallel σ^o substituent constants for these heterocyclic groups have been reported from work on the gas–phase eliminations of t–butyl heteroarylcarboxylate esters.[7] The Hammett ρ–value (0.23 at 600 K) used here in computing the substituent constants of the heterocyclic groups is that derived for the gas–phase elimination reaction of the isopropyl phenylethanoate ester.[10] The rationale for using this reaction constant, and for adopting the phenylethanoate molecular frame as a model for the heteroarylcarboxylate esters under study, has been explained.[1,7]

The Arrhenius energies and entropies of activation are in agreement with the cyclic transition state proposed for these reaction pathways. The transition state of these reactions is held to be semi–concerted with partial negative charge development at the carbonyl carbon atom of the carboxylate group.[2,3] It follows, therefore, that substituents at this centre capable of negative charge dispersal would enhance substrate reactivity relative to substituents less capable of such

Table 1. Rate Coefficients ($10^3k/s^{-1}$) for (Hetero)aryl GCO_2CHMe_2 Ester Pyrolysis.

G =	Phenyl		2–Thienyl		3–Thienyl		2–Furyl	
	T/K	k	T/K	k	T/K	k	T/K	k
	633	5·27	635	8·06	640	7·80	626	4·40
	635	6·25	638	9·54	641	8·26	633	6·54
	642	9·29	647	15·74	649	12·88	637	8·17
	644	10·40	656	25·53	650	13·61	642	10·78
	650	14·45	661	33·22	660	23·36	647	14·13
	653	17·02	665	40·90	667	33·88	650	16·57
	660	24·72	669	50·23	676	53·70	656	22·78
	662	27·48	675	68·06	678	59·43	668	42·20
	669	39·36	684	106·30	685	84·20	669	44·38
	670	41·69	693	164·10	686	88·51	677	66·07
	678	62·37			692	118.6	686	102·2
	679	65·56			697	150·8	693	142·4
	688	102·3						
	689	107·4						

G=	3–Furyl		3–Pyridyl		4–Pyridyl	
	T/K	k	T/K	k	T/K	k
	643	8·83	631	5·99	636	9·20
	646	10·47	635	7·41	638	10·31
	652	14·62	641	10·12	646	15·81
	661	23·81	650	16.22	647	16·68
	664	27·94	652	17·98	654	24·18
	671	40·37	657	23·23	657	27·61
	674	47·16	664	32·95	662	35·48
	679	60·93	670	43·81	664	37·58
	684	78·52	672	48·75	670	52·60
	688	95·72	677	60·81	676	69·21
	697	148·6	683	80·77	679	80·97
	704	207·5	686	94·67	681	89·95
			694	136·7	689	129·1

Table 2. Arrhenius Parameters and Rate Data and σ^0 Values at 600 K for Pyrolysis of (Hetero)aryl GCO_2CHMe_2 Esters.

G	log $\underline{A}/s^{-1}$	$\underline{E_a}/kJ\ mol^{-1}$	$\Delta S^{\ddagger}/J\ mol^{-1}\ K^{-1}$	Corr. coef.
(1) Phenyl	13·66	192·80	10·8	1.000
(2) 2–Thienyl	13·20	186·15	1·97	0·999
(3) 3–Thienyl	13·62	192·67	10·0	1·000
(4) 2–Furyl	13·25	186·98	2·93	1·000
(5) 3–Furyl	13·76	194·64	12·7	1·000
(6) 3–Pyridyl	12.80	181·46	–5·69	1·000
(7) 4–Pyridyl	12·90	181·79	–3·96	0·999

G	$10^5k/s^{-1}$	log K_{rel}	σ^0	
			(a)	(b)
(1)	75·34			
(2)	100·0	0·123	0·53	0·50
(3)	70·46	–0·029	–0·13	0·04 (±0·08)
(4)	94·03	0·096	0·42	0·41
(5)	65·58	–0·060	–0·26	0·04 (±0·08)
(6)	100·9	0·127	0·55	0·53 (0·72)
(7)	120·2	0·203	0·88	0·85 (0·94)

(a) This study. (b) Literature values for reactions in solution.

electron–withdrawing facility.

The greater activating power of the 2–position over the 3–position in the five–membered ring is expected from the proximity in the former of the electronegative heteroatom to the centre of negative charge being developed in the transition state of the reaction. On the other hand, the order of relative reactivities of the equivalent positions in furan and thiophene can be considered as a net product of the mesomeric and inductive effects characteristic of the O and S heteroatoms. Both atoms are capable of +M and –I effects. However, the S atom with its empty 3d–orbit would be expected to surpass O in its ability to accommodate better the negative charge being developed. This latter effect would tend to make the thienyl group more activating than the furyl group. The electronic effects of these substituents are reflected in both the sign and magnitude of the group's σ^{0}–values.

In pyridine, the mesomeric and inductive effects of the nitrogen heteroatom are reinforcing. The result is that the 4–position in pyridine becomes more activating than the 3–position, since resonance interactions at the latter position are minimal.

The Hammett σ^{0}–values obtained on the basis of the present kinetic results are identical with those computed for the t–butyl heteroarylcarboxylate esters,[7] and are in good agreement with replacement σ^{0}–values obtained from reactions in solution.[4-6] It is to be noted, however, that gas–phase reactions are less susceptible to media effects than reactions in solution.

Experimental

Reaction Kinetics and Product Analysis.— The techniques used for measuring rates and for analyzing kinetic data are reported elsewhere. The procedures for collecting, analyzing and identifying the products of the elimination reactions, together with the data on the products identified, are the same as those reported for the t–butyl heteroarylcarboxylate esters.[1,11]

Materials.— Isopropyl benzoate, nicotinate, and isonicotinate were obtained from the laboratory of Dr. R. Taylor (Sussex University, U.K.); the samples were purified by fractional distillation, and their identity substantiated by chemical analysis (Malissa and Reuter Analytische Laboratorien, Gummersbach 1 Elbach, West Germany). The remaining heteroarylcarboxylates were prepared from the corresponding carboxylic acids obtained commercially, and following suitable literature procedures.[12-14] The acids were converted into acid chlorides, which were then heated under reflux with sodium isopropoxide. Normal work–up followed by fractional distillation yielded the following esters:

isopropyl 2–thienoate (69%), b.p. 63 °C at 0.9 mmHg, δ ($CDCl_3$) 7.5–7.7 (1 H, d, H–5), 7.3–7.5 (1 H, d, H–3), 6.8–7.0 (1 H, t, H–4), 4.9–5.4 (1 H, m, $HCMe_2$), 1.3 (6 H, d, $HCMe_2$), (Found: C, 55.54; H, 5.83; S, 17.89 $C_8H_{10}O_2S$ requires C, 56.44; H, 5.93; S, 18.83%); isopropyl 3–thienoate (65%), b.p. 60 °C at 0.9 mmHg, δ ($CDCl_3$) 8.0 (1 H, s, H–2), 7.4 (1 H, d, H–5), 7.0–7.2 (1 H, m, H–4), 4.9–5.4 (1 H, m, $HCMe_2$), 1.3 (6 H, d, $HCMe_2$), (Found: C, 55.80; H, 5.78; S, 17.74%); isopropyl 2–furoate (60%), b.p. 56 °C at 1.0 mmHg, δ ($CDCl_3$) 7.6 (1 H, s, H–5), 7.0 (1 H, d, H–3), 6.6 (1 H, m, H–4), 4.9–5.4 (1H, m, $HCMe_2$), 1.3 (6 H, d, $HCMe_2$), (Found: C, 61.94; H, 6.50. $C_8H_{10}O_3$ requires C, 62.32; H, 6.55%); isopropyl 3–furoate (41%) b.p. 36 °C at 1.0 mmHg, δ ($CDCl_3$) 8.0 (1 H, s, H–2), 7.4 (1 H, d, H–5), 6.6 (1 H, m, H–4), 4.9–5.4 (1 H, m, $HCMe_2$), 1.3 (6 H, d, $HCMe_2$), (Found: C, 61.59, H, 6.56%).

Acknowledgements

This work was supported by Kuwait University through research grant SC032. The authors wish to thank Dr. R. Taylor for samples of isopropyl benzoate, nicotinate, and isonicotinate, and for his interest and valuable comments.

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