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THEORETICAL STUDIES OF SUBSTITUENT EFFECTS ON THERMAL ELIMINATIONS OF ARYL ETHYL CARBONATES AND *S*-ARYL *O*-ETHYL THIOCARBONATES*

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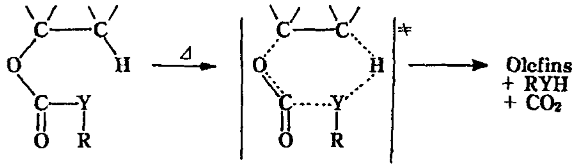
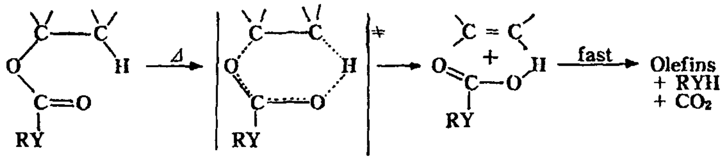
Substituent effects on the thermal elimination reactions of carbonates and thiocarbonates were investigated MO theoretically using the AM1 method. For both substrates, an electron-withdrawing group is found to facilitate the decomposition. A two-step process is favoured by carbonates, whereas one- and two-step processes can compete in the pyrolysis of thiocarbonates. The ability to transmit substituent effect is greater with oxygen (carbonates) than with sulphur (thicarbonates) in contrast to the experimental results of Taylor and co-workers. Modelling studies with replacement of the phenyl ring with a vinyl group are found to be justified in this type of work.

INTRODUCTION

Two reaction pathways, (1) and (2), are proposed for gas-phase thermal elimination reactions of carbonates producing olefins, alcohols (or phenol) and carbon dioxide (if no β-hydrogen atom is present, decomposition may also occur, but at much higher temperatures and the products are often complex[1]). In the two-step mechanism, equation (2), the hydrogen carbonate is initially eliminated by a mechanism formally similar to that of carboxylic ester pyrolysis.[2] The hydrogen carbonate is then assumed to decompose rapidly in a subsequent step. In contrast, in the one-step mechanism, equation (1), all three products are formed simultaneously.[3] It has been reported that the one-step mechanism cannot be entirely ruled out,[4] although results of experimental[5] and theoretical[8] studies seem to favour the two-step pathway as a more plausible mechanism. Substituent effect studies on the aryl ethyl carbonates (**I**; Y = O and R = C_6H_4X) by Smith *et al.*[7] and on the *S*-aryl *O*-ethyl thiocarbonates (**II**; Y = S and R = C_6H_4X) by Al-Awadi and Taylor[8] have shown that the rates of thermal decomposition of these compounds are accelerated by an electron-withdrawing group.



(1)



(2)

(where R denotes alkyl– or aryl–group)

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According to the results of these studies, the Hammett coefficient ρ obtained with the Taft σ° values[9] were 0·2 and 0·3 at 600 K for carbonates and thiocarbonates, respectively, indicating that sulphur has a relatively greater ability than oxygen to transmit electronic effects in the gas phase. This is in contrast to the opposite trend reported by Marcus *et al.*[10]

In this work, we set out to shed some light on this controversial problem through MO theoretical substituent effect studies of aryl ethyl carbonates (**I**) and *S*-aryl *O*-ethyl thiocarbonates (**II**) with *para* substituents (X = NH_2, CH_3, H, F and NO_2) in the aryl group, R, in pathways (1) and (2). In addition, we tested the feasibility of model studies by using a vinyl group, XHC=CH—, in the place of aryl groups, *p*-XC_6H_4—, in both series of compounds.

CALCULATIONS

The AM1 procedure[11] was used throughout. The ground states (geometries and energies) were fully optimized with respect to all geometrical parameters and characterized by all positive eigenvalues in the Hessian matrix.[12] Transition states were located by the reaction coordinate method,[13] refined by the gradient norm minimization method[14] (using the NLLSQ or SIGMA option implemented in the AMPAC package), and characterized by confirming only one negative eigenvalue in the Hessian matrix.[12]

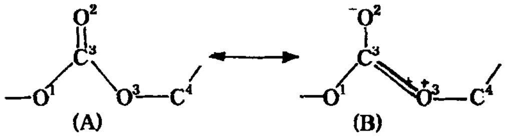
RESULTS AND DISCUSSION

Aryl ethyl carbonates (I)
$p-XC_6H_4—O^1—C^1(=O^2)—O^3—C^2H_2—C^3H_3$

Heats of formation (ΔH_f) of ground (GS) and transition (TS) states and enthalpies of activation ($\Delta H^{\ast}$) for thermal eliminations of aryl ethyl carbonates (**I**) are summarized in Table 1 for both pathways (1) and (2).

The data reveal that the activation barrier is favoured (and hence the elimination rate increases) by a more electron-withdrawing group (e.g. X = *p*-NO_2) for both reaction pathways. This reactivity trend appears contrary to what one would expect from a decrease in positional charge density at the carbonyl oxygen, O^2, for pathway (2) and the ether oxygen, O^1, for pathway (1) owing to the $-I$ effect, i.e. electron-withdrawing inductive effect, of the *para* substituent. In fact, however, the positional charge densities in Table 2 indicate that the negative charge increment in the activation, Δq, on O^1 as well as on O^2 become larger with increase in the electron-withdrawing power of the *para* substituent. This increase in the positional charge density in the TS with the $-I$ effect of X may be ascribed to the greater contribution of the p–π conjugation[15] between O^3 and $C^1=O^2$, as represented by a resonance structure (B) in Scheme 1, in the TS compared with that in the GS; negative charge build-up in the TS at the oxygen atoms for the nucleophilic attack on migrating hydrogen atom is thus facilitated by the $-I$ effect of X. However, the degree of bond breaking of the $C^3—H$ bond in the TS and hence the degree of bond formation between H and O^2 [path (2)] or O^1 [path (1)] decrease with the electron-withdrawing power of X, as shown by the bond distance changes in Table 3. Bond distances of the $C^2—C^3$ and $C^1—O^3$ bonds exhibit little variation with the substituent X; in contrast, the degree of bond breaking of the $C^2—O^3$ bond increase with the $-I$ effect of X due to the greater bond-weakening effect arising from the greater contribution of resonance structure (B) in Scheme 1.

These bond distance changes indicate that bond scission of $C^2—O^3$ takes place at an earlier stage of the reaction with little effect on the activation barrier; thus the important rate-limiting step is the $C^3—H$ bond scission (or the nucleophilic attack of H by O^2 or O^1) since a lesser degree of bond cleavage in the TS for a more electron-withdrawing group X should require less energy, i.e. a lower activation energy barrier. This con-



Scheme 1

Table 1. Heats of formation, ΔH_f, of the GS and TS, and the activation enthalpies, $\Delta H^{\ast}$, for the thermal decompositions of aryl ethyl carbonates (**I**) in kcal mol^{-1}

X	GS	TS(1)[a]	TS(2)[a]	$\Delta H^{\ast}(1)$[a]	$\Delta H^{\ast}(2)$[a]
NH_2	−103·5	−32·5(−1876·7)[b]	−46·3(−1685·1)	71·0	57·2
CH_3	−109·5	−38·7(−1868·9)	−52·5(−1669·1)	70·8	57·0
H	−101·8	−31·1(−1872·6)	−44·8(−1667·1)	70·7	57·0
F	−146·6	−75·9(−1839·8)	−89·7(−1549·4)	70·7	56·9
NO_2	−96·7	−27·8(−1893·0)	−41·5(−1649·3)	68·9	56·1

[a] The numbers in parentheses denote the pathway.
[b] Imaginary vibrational frequency (ν_i) at TS in cm^{-1}.

Table 2. Positional charge densities (q) in the GS and TS for the thermal decompositions for aryl ethyl carbonates (**I**) in electronic charge units

X		O^1	C^1	O^2	O^3	C^2	C^3	$H(C^3)$
NH_2	GS	−0·172	+0·395	−0·384	−0·232	−0·009	−0·250	+0·099
	TS(1)[a]	−0·289	+0·433	−0·377	−0·481	+0·159	−0·475	+0·358
	TS(2)	−0·189	+0·436	−0·412	−0·394	+0·144	−0·557	+0·352
	Δq[b](1)	−0·117	+0·038	+0·007	−0·249	+0·168	−0·225	+0·259
	Δq(2)	−0·017	+0·041	−0·028	−0·162	+0·153	−0·307	+0·253
CH_3	GS	−0·177	+0·398	−0·380	−0·231	−0·009	−0·250	+0·099
	TS(1)	−0·301	+0·436	−0·375	−0·483	+0·161	−0·469	+0·359
	TS(2)	−0·195	+0·431	−0·410	−0·392	+0·136	−0·539	+0·346
	Δq(1)	−0·123	+0·038	+0·005	−0·252	+0·170	−0·219	+0·260
	Δq(2)	−0·018	+0·033	−0·030	−0·161	+0·145	−0·289	+0·247
H	GS	−0·178	+0·398	−0·380	−0·231	−0·009	−0·251	+0·099
	TS(1)	−0·303	+0·437	−0·375	−0·483	+0·162	−0·468	+0·360
	TS(2)	−0·196	+0·439	−0·412	−0·392	+0·145	−0·554	+0·351
	Δq(1)	−0·125	+0·039	+0·005	−0·252	+0·171	−0·217	+0·261
	Δq(2)	−0·018	+0·041	−0·032	−0·161	+0·154	−0·303	+0·252
F	GS	−0·176	+0·398	−0·379	−0·229	−0·009	−0·251	+0·099
	TS(1)	−0·307	+0·438	−0·376	−0·484	+0·166	−0·464	+0·360
	TS(2)	−0·196	+0·439	−0·421	−0·399	+0·150	−0·544	+0·352
	Δq(1)	−0·131	+0·040	+0·003	−0·255	+0·175	−0·213	+0·261
	Δq(2)	−0·020	+0·043	−0·042	−0·170	+0·159	−0·293	+0·253
NO_2	GS	−0·178	+0·402	−0·372	−0·224	−0·009	−0·252	+0·099
	TS(1)	−0·337	+0·449	−0·371	−0·488	+0·179	−0·448	+0·364
	TS(2)	−0·208	+0·440	−0·451	−0·429	+0·165	−0·492	+0·351
	Δq(1)	−0·159	+0·047	+0·001	−0·264	+0·188	−0·196	+0·265
	Δq(2)	−0·030	+0·038	−0·079	−0·205	+0·174	−0·240	+0·252

[a] The numbers in parentheses denote the pathway.
[b] $\Delta q = q(\mathrm{TS}) - q(\mathrm{GS})$.

Table 3. Selected bond lengths (d) in the GS and TS for the thermal decompositions for aryl ethyl carbonates (**I**) in Å

X		O^1—C^1	C^1—O^2	C^1—O^3	O^3—C^2	C^2—C^3	C^3—H	H—O[b]
NH_2	GS	1·363	1·228	1·356	1·443	1·507	1·118	—
	TS(1)[a]	1·471	1·222	1·262	2·059	1·391	1·366	1·299
	TS(2)	1·361	1·287	1·276	1·845	1·404	1·394	1·241
	Δd[c](1)	+0·108	−0·006	−0·094	+0·616	−0·116	+0·248	—
	Δd(2)	−0·002	+0·059	−0·080	+0·402	−0·103	+0·276	–
CH_3	GS	1·363	1·227	1·355	1·443	1·507	1·118	—
	TS(1)	1·474	1·222	1·261	2·076	1·390	1·359	1·311
	TS(2)	1·361	1·285	1·275	1·853	1·404	1·386	1·252
	Δd(1)	+0·111	−0·005	−0·094	+0·633	−0·117	+0·241	—
	Δd(2)	−0·002	+0·058	−0·079	+0·410	−0·103	+0·268	—
H	GS	1·363	1·227	1·355	1·443	1·507	1·118	—
	TS(1)	1·474	1·221	1·260	2·080	1·390	1·359	1·313
	TS(2)	1·362	1·286	1·275	1·846	1·404	1·389	1·244
	Δd(1)	+0·111	−0·006	−0·095	+0·637	−0·117	+0·241	—
	Δd(2)	−0·001	+0·059	−0·080	+0·403	−0·103	+0·271	—
F	GS	1·365	1·226	1·354	1·444	1·507	1·118	—
	TS(1)	1·478	1·221	1·259	2·098	1·390	+1·353	1·324
	TS(2)	1·365	1·284	1·273	1·869	1·404	1·376	1·261
	Δd(1)	+0·113	−0·005	−0·095	+0·654	−0·117	+0·235	—
	Δd(2)	0·000	+0·058	−0·081	+0·452	−0·103	+0·258	—
NO_2	GS	1·368	1·226	1·352	1·446	1·507	1·118	—
	TS(1)	1·494	1·220	1·253	2·162	1·389	1·332	1·365
	TS(2)	1·373	1·278	1·267	1·982	1·400	1·326	1·350
	Δd(1)	+0·126	−0·006	−0·099	+0·716	−0·118	+0·214	—
	Δd(2)	+0·005	+0·052	−0·085	+0·536	−0·107	+0·208	—

[a] The numbers in parentheses denote the pathway.
[b] $d(O^2$—H) in TS(2) and $d(O^1$—H) in TS(1).
[c] $\Delta d = d(\mathrm{TS}) - d(\mathrm{GS})$.

Table 4. Heats of formation, ΔH_f, of the GS and TS, and the activation enthalpies, $\Delta H^{\neq}$, for the thermal decompositions of β-X-vinyl ethyl carbonates (**III**) in kcal mol^{-1}

X	GS	TS(1)[a]	TS(2)[a]	$\Delta H^{\neq}$(1)[a]	$\Delta H^{\neq}$(2)[a]
NH_2	−117·6	−47·1(−1844·8)[b]	−60·7(−1684·5)	70·5	56·9
CH_3	−123·2	−53·5(−1880·4)	−66·8(−1671·7)	69·7	56·4
H	−113·4	−43·7(−1883·7)	−57·1(−1678·6)	69·7	56·3
F	−161·5	−91·5(−1890·0)	−105·4(−1627·4)	70·0	56·1
NO_2	−111·2	−44·0(−1636·6)	−57·2(−1341·2)	68·2	54·0

[a] The numbers in parentheses denote the pathway.
[b] Imaginary vibrational frequency (ν_i) at TS in cm^{-1}.

clusion is consistent with our previous results on the pyrolysis mechanism of carboxylic esters.[16]

On the other hand, comparison of activation enthalpies between the two reaction pathways show that for the gas-phase thermal elimination of aryl ethyl carbonates (**I**) the two-step mechanism [equation (2)], has lower activation barrier by *ca* 14 kcal mol^{-1} (1 kcal = 4·184 kJ) than the one-step mechanism [equation (1)]. Mechanism (2) is favoured because (i) in this mechanism the nucleophile is the carbonyl oxygen, O^2, whereas in mechanism (1) it is the ether oxygen, O^1, which is less nucleophilic (Table 2), and (ii) in mechanism (2) two σ-bonds (O^3—C^2 and C^3—H) and one π-bond (C^1—O^2) break but in return one σ-bond (O^2—H) and two π-bonds (C^1—O^3 and C^2—C^3) are newly formed, whereas in mechanism (1) three σ-bonds (O^1—C^1, O^3—C^2 and C^3—H) break with the same number of bond formations as in mechanism (2). This means that an additional σ-bond cleavage is required, which should lead to correspondingly higher activation energy in pathway (1).

The results of modelling by replacing a phenyl group (XC_6H_4—) with a vinyl group (XCH=CH—) are very similar. In comparisons of $\Delta H^{\neq}$ (Tables 1 and 4) for **I** and **III**, for example, both systems reveal that they differ very little and show identical trends. The individual values and the trends of changes for positional charge densities (*q*) and bond lengths (*d*) due to substituents for β-substituted vinyl ethyl carbonates (**III**) are also very similar and indeed show that the modelling study of **I** using **III** can be deemed a realistic one. This success may be attributed to the fact that the phenyl or vinyl group does not itself constitute a reaction centre but only plays a role of a substituent attached to C^1 or O^1. Nevertheless, the results of the present modelling studies provide a good basis for such an approximation.

S-Aryl O-ethyl thiocarbonates (II)
p-XC_6H_4—S^1—C^1(=O^2)—O^3—C^2H_2—C^3H_3

The heats of formation, ΔH_f, of the GS and TS and the enthalpies of activation, $\Delta H^{\neq}$, for thermal elimination of *S*-aryl *O*-ethyl thiocarbonates (**II**) are summarized in Table 5. The activation enthalpies are seen to decrease, and hence the reactivity increases, with a more electron-withdrawing substituent in the aryl group, e.g. X = p-NO_2, which is similar to the trend found for **I** above. This is consistent with the experimental results of Al-Awadi and Taylor.[8] Strikingly, however, in the reactions of thiocarbonates (**II**), the two-step process is unfavourable by *ca* 4 kcal mol^{-1} whereas the one-step process is more favourable by *ca* 4–6 kcal mol^{-1} compared with the corresponding process for carbonates (**I**) (Table 1).

The former difference in the reactivity for the two-step processes of **I** and **II** arises in fact from the differences in polar and resonance effects between O and S; in the two-step mechanism the *Y*-aryl group is substituent attached to C^1 and the *O*-aryl group should be more electron attracting than the *S*-aryl group since the

Table 5. Heats of formation, ΔH_f, of the GS and TS, and the activation enthalpies, $\Delta H^{\neq}$, for the thermal decompositions of *S*-aryl *O*-ethyl thiocarbonates (**II**) in kcal mol^{-1}

X	GS	TS(1)[a]	TS(2)[a]	$\Delta H^{\neq}$(1)[a]	$\Delta H^{\neq}$(2)[a]
NH_2	−53.9	11.0(−1870.5)[b]	7.1(−1033.6)	64.9	61.0
CH_3	−59.3	5.5(−1908.1)	1.6(−1014.6)	64.8	60.9
H	−51.5	13.2(−1914.5)	9.4(−1005.5)	64.7	60.9
F	−96.5	−31.9(−1936.2)	−35.7 (−978.9)	64.6	60.8
NO_2	−46.8	17.2(−1956.8)	13.6 (−887.2)	64.0	60.4

[a] The numbers in parentheses denote the pathway.
[b] Imaginary vibrational frequency (ν_i) at TS in cm^{-1}.

electronegativity of O is greater than that of S (Taft's $\sigma^* = 2\cdot43$ and $1\cdot87$ for *O*-phenyl and *S*-phenyl, respectively)[17] so that the p–π conjugation in Scheme 1 should play a greater role in the *O*-aryl compound. In the one-step mechanism, however, the Y atom constitutes an integral part of the reaction centre within the six-membered cyclic TS; the C^1—Y bond cleaves while the Y—H bond is formed so that the bond strength of the C^1—Y bond and the nucleophilicity of Y should play an important role in determining the difference in reactivity. The bond energy[18] of C—O is *ca* 85–91 kcal mol^{-1} whereas that of C—S is *ca* 66 kcal mol^{-1} so that the thiocarbonates should be more reactive in the one-step mechanism. On the other hand, the lone pair orbital (n) on S is higher than that on O so that the interaction between the n and σ^* orbitals of H—C^3 should be more stabilizing [$\Delta\varepsilon_{FMO} = \varepsilon(\sigma^*) - \varepsilon(n) = 20\cdot43$ and $20\cdot26$ eV for carbonates (X = H) **I** and **III**, respectively, and $14\cdot27$ and $14\cdot24$ eV for thiocarbonates (X = H) **II** and **IV**, respectively]. Owing to these favourable factors for the one-step mechanism, thiocarbonates have lower activation barriers than carbonates. Notwithstanding these differences, for thiocarbonates also the two-step mechanism is more favoured than the one-step mechanism for similar reasons to those discussed above for carbonates. For the carbonates, however, the differences in activation enthalpies between the two mechanisms were *ca* 14 kcal mol^{-1}, in contrast to the mere 4 kcal mol^{-1} for the thiocarbonates; this suggests that for the thiocarbonates the one-step mechanism cannot be entirely ruled out and the two mechanisms may well be competing in real reaction systems.

The positional charge densities and selected bond lengths for the GS and TS of the pyrolysis of thiocarbonates (**II**) are presented in Tables 6 and 7. The data reveal that the general trends in these quantities are similar to those for carbonates in Tables 2 and 3. The results of replacing the aryl group, *p*-C_6H_4—, by a vinyl group, XCH=CH—, to form XCH=CH—S—C(=O)—O—CH_2CH_3 (**IV**) show very little differences and trends in $\Delta H^{\ddagger}$, positional charge densities and bond lengths from the corresponding values for **II**, as discussed for **I** and **III**. This again confirms that the modelling of **I** and **II** can be achieved by using a vinyl group, XCH=CH— in place of an aryl group, *p*-XC_6H_4— (**III** and **IV**, respectively) in the studies of the substituent effect on the reactivity of gas-phase thermal decomposition. The heats of formation, ΔH_f, of the GS and TS and the enthalpies of activation,

Table 6. Positional charge densities (*q*) in the GS and TS for the thermal decompositions for *S*-aryl *O*-ethyl thiocarbonates (**II**) in electronic charge units

X		S^1	C^1	O^2	O^3	C^2	C^3	$H(C^3)$
NH_2	GS	+0·316	+0·163	−0·356	−0·257	−0·012	−0·245	+0·096
	TS(1)[a]	+0·043	+0·326	−0·356	−0·471	+0·148	−0·427	+0·265
	TS(2)	+0·282	+0·188	−0·379	−0·371	+0·117	−0·549	+0·338
	Δq[b](1)	−0·273	+0·163	0·000	−0·214	+0·160	−0·182	+0·169
	Δq(2)	−0·034	+0·025	−0·023	−0·114	+0·129	−0·304	+0·242
CH_3	GS	+0·314	+0·165	−0·354	−0·256	−0·012	−0·245	+0·096
	TS(1)	+0·029	+0·331	−0·351	−0·469	+0·151	−0·426	+0·267
	TS(2)	+0·273	+0·192	−0·385	−0·376	+0·120	−0·537	+0·338
	Δq(1)	−0·285	+0·118	+0·003	−0·213	+0·163	−0·181	+0·171
	Δq(2)	−0·041	+0·027	−0·031	−0·120	+0·132	−0·292	+0·242
H	GS	+0·313	+0·165	−0·353	−0·255	−0·012	−0·246	+0·096
	TS(1)	+0·024	+0·332	−0·350	−0·469	+0·153	−0·426	+0·268
	TS(2)	+0·271	+0·193	−0·386	−0·377	+0·120	−0·535	+0·338
	Δq(1)	−0·289	+0·167	+0·003	−0·214	+0·165	−0·180	+0·172
	Δq(2)	−0·042	+0·028	−0·033	−0·122	+0·132	−0·289	+0·242
F	GS	+0·319	+0·165	−0·353	−0·254	−0·012	−0·246	+0·096
	TS(1)	+0·019	+0·336	−0·350	−0·467	+0·156	−0·424	+0·268
	TS(2)	+0·272	+0·195	−0·394	−0·382	+0·124	−0·527	+0·339
	Δq(1)	−0·300	+0·171	+0·003	−0·213	+0·168	−0·178	+0·172
	Δq(2)	−0·047	+0·030	−0·041	−0·128	+0·136	−0·281	+0·243
NO_2	GS	+0·330	+0·168	−0·349	−0·250	−0·012	−0·247	+0·096
	TS(1)	−0·025	+0·355	−0·337	−0·460	+0·169	−0·419	+0·273
	TS(2)	+0·262	+0·206	−0·416	−0·401	+0·139	−0·498	+0·340
	Δq(1)	−0·355	+0·187	+0·012	−0·210	+0·181	−0·172	+0·177
	Δq(2)	−0·068	+0·038	−0·067	−0·151	+0·151	−0·251	+0·244

[a] The numbers in parentheses denote the pathway.

[b] $\Delta q = q(TS) - q(GS)$

Table 7. Selected bond lengths (*d*) in the GS and TS for the termal decompositions for *S*-aryl *O*-ethyl thiocarbonates (**II**) in Å

X		S^1—C^1	C^1—O^2	C^1—O^3	O^3—C^2	C^2—C^3	C^3—H	H—O^b
NH_2	GS	1·709	1·234	1·363	1·437	1·508	1·117	—
	TS(1)^a	1·894	1·225	1·261	2·085	1·395	1·319	1·657
	TS(2)	1·710	1·299	1·288	1·790	1·406	1·422	1·204
	Δd^c(1)	+0·185	−0·009	−0·102	+0·648	−0·113	+0·202	—
	Δ*d*(2)	+0·001	+0·065	−0·075	+0·353	−0·102	+0·305	—
CH_3	GS	1·709	1·234	1·363	1·438	1·508	1·117	—
	TS(1)	1·901	1·224	1·260	2·089	1·395	1·316	1·661
	TS(2)	1·712	1·297	1·286	1·811	1·405	1·407	1·221
	Δ*d*(1)	+0·192	−0·010	−0·103	+0·651	−0·113	+0·199	—
	Δ*d*(2)	+0·003	+0·063	−0·077	+0·373	−0·103	+0·290	—
H	GS	1·709	1·234	1·363	1·438	1·508	1·117	—
	TS(1)	1·902	1·224	1·260	2·089	1·396	1·314	1·663
	TS(2)	1·713	1·297	1·286	1·814	1·405	1·405	1·224
	Δ*d*(1)	+0·193	−0·010	−0·103	+0·651	−0·112	+0·197	−
	Δ*d*(2)	+0·004	+0·063	−0·077	+0·376	−0·103	+0·288	—
F	GS	1·710	1·234	1·361	1·438	1·508	1·117	—
	TS(1)	1·907	1·224	1·259	2·094	1·396	1·310	1·669
	TS(2)	1·715	1·295	1·285	1·834	1·405	1·392	1·239
	Δ*d*(1)	+0·197	−0·010	−0·102	+0·656	−0·112	+0·193	—
	Δ*d*(2)	+0·005	+0·061	−0·076	+0·396	−0·103	+0·275	—
NO_2	GS	1·712	1·234	1·360	1·440	1·508	1·117	—
	TS(1)	1·934	1·221	1·255	2·106	1·398	1·294	1·690
	TS(2)	1·723	1·291	1·279	1·904	1·403	1·354	1·293
	Δ*d*(1)	+0·222	−0·013	−0·105	+0·666	−0·110	+0·177	—
	Δ*d*(2)	+0·011	+0·057	−0·081	+0·464	−0·105	+0·237	—

[a] The numbers in parentheses denote the pathway.
[b] *d*(O^2—H) in TS(2) and *d*(S^1—H) in TS(1).
Δ*d* = *d*(TS) − *d*(GS).

Table 8. Heats of formation, ΔH_f, of the GS and TS, and the activation enthalpies, $\Delta H^{\neq}$, for the thermal decompositions of β-X-*S*-vinyl *O*-ethyl thiocarbonates (**IV**) in kcal mol^{-1}

X	GS	TS(1)^a	TS(2)^a	$\Delta H^{\neq}(1)^a$	$\Delta H^{\neq}(2)^a$
NH_2	−68·3	−3·1(−1882·2)^b	−7·6(−1047·9)	65·2	60·7
CH_3	−72·3	−7·0(−1921·3)	−12·0(−1013·2)	65·3	60·3
H	−62·2	3·0(−1931·5)	−1·9 (−999·6)	65·2	60·3
F	−111·5	−46·4(−1958·1)	−51·4 (−963·4)	65·1	60·1
NO_2	−59·9	4·3(−1884·8)	−0·9 (−776·1)	64·2	59·0

[a] The numbers in parentheses denote the pathway.
[b] Imaginary vibrational frequency (ν_i) at TS in cm^{-1}.

$\Delta H^{\neq}$, for thermal elimination of *S*-vinyl *O*-ethyl thiocarbonates (**IV**) are summarized in Table 8.

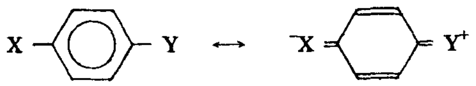
Comparison of transmitting ability between O and S

Our AM1 results for substituent effects on thermal eliminations of carbonates and thiocarbonates are found to agree well with those of the gas-phase experiments with one exception: Taylor and co-workers[7,8] found experimentally that sulphur (Y = S; $\rho = 0{\cdot}30$ at 600 K) is a better transmitter of the substituent (X) effect than oxygen (Y = O; $\rho = 0{\cdot}20$ at 600 K) in the —YC_6H_4X group, in contrast to our theoretical results shown in Table 9. The ρ values in this table are evaluated by plotting $-\Delta H^{\neq}/2.3RT$ versus σ. We determined two types of ρ values, ρ^0 and ρ^-, by employing σ^0, a universal substituent constant,[19] and σ^- values.[20] The substituent constant σ^0 is thought to reflect mainly transmission of electrons by π-polarization, which is neither pure resonance nor σ-inductive effects, whereas σ^- reflects strong resonance effect by through conjugation (Scheme 2).

Table 9. Slopes ρ of $-\Delta H^{\ddagger}/2{\cdot}3RT$ values σ with σ^0 and $\sigma^{-\text{a}}$

X	σ^0	σ^-	ρ^0	ρ^-
p-NH_2	−0·30	−0·66		
p-CH_3	−0·14	−0·17		
H	0·00	0·00		
p—F	0·15	0·02		
p—NO_2	0·81	1·27		
Aryl ethyl (**I**)	Pathway (1)		1·93 (r = 0·963)[b]	1·17 (r = 0·968)
	Pathway (2)		0·98 (r = 0·983)	0·59 (r = 0·986)
S-Aryl *O*-ethyl (**II**)	Pathway (1)		0·82 (r = 0·997)	0·49 (r = 0·985)
	Pathway (2)		0·54 (r = 0·990)	0·32 (r = 0·982)

[a] Taken from Refs 19 and 20.
[b] r = Correlation coefficient.



Scheme 2

Reference Table 9 reveals (i) in all cases the ρ values are greater with Y = O rather than Y = S, indicating oxygen is the better transmitter; (ii) the ρ values are greater for pathway (1) than for pathway (2), which correctly reflects that Y is directly involved in the cyclic TS in pathway (1) in contrast to the indirect involvement in pathway (2); and (iii) for Y = S linearity is better with σ^0 whereas for Y = O linearity is better with σ^- (Scheme 2), suggesting that oxygen is a much better transmitter of the substituent (X) effect in both types of mechanisms.

Since in the gas-phase eliminations of carbonates and thiocarbonates the entropy factor should vary little in the activation process depending on different substituents X, we believe that the use of $\Delta H^{\ddagger}$ instead of $\Delta G^{\ddagger}$ is justified in determining ρ values. Hence we can consider the following probable causes for the discrepancy between the experimental and theoretical trends in ρ values. First, the experimental ρ values at 600 K may well be on the borderline of experimental uncertainty in view of the small difference of 0·1 in ρ (ρ = 0·3 for Y = S versus 0·2 for Y = O). Second, different thermal decomposition mechanisms may apply to carbonates and thiocarbonates. We have seen above that for thiocarbonates the two mechanisms, one-step and two-step, can in fact compete whereas for carbonates the two-step mechanism is predominant. Moreover, MO theoretically, the overlap and hence the electron transmission between adjacent carbon and oxygen atoms should be greater than that between carbon and sulphur atoms, since overlap between two second-row elements (C and O) should be greater than that between second- and third-row elements (C and S). (Although the diatomic differential overlaps are neglected in the AM1 method, the resonance integrals can represent the similar concept and quantity in this case.)

We can summarize our results as follows. Carbonates are more reactive than thiocarbonates in the thermal decomposition reaction. Carbonates prefer to pyrolyze by a two-step mechanism whereas two types of mechanisms, one-step and two-step, can compete in the pyrolysis of thiocarbonates. An electron-withdrawing substituent (X) in the aryl group facilitates thermal decomposition of both carbonates and thiocarbonates by stabilizing the negative charge formed in the reaction centre by the p—π conjugation effect in the TS. The ability to transmit substituent effect is greater with Y = O than with Y = S. The modelling study by replacing a phenyl ring with a vinyl group is justified in the present type of theoretical work.

Supplementary material

The positional charge densities and selected bond lengths for the GS and TS of the pyrolysis of vinyl ethyl carbonates (**III**) and *S*-vinyl *O*-ethyl thiocarbonates (**IV**) and are available from the authors on request.

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