The Mechanism of Thermal Eliminations. Part 19.[1] Rate Data for Pyrolysis of *S*-Aryl *O*-Ethyl Thiocarbonates: the Relative Abilities of Oxygen and Sulphur to Transmit Electronic Effects

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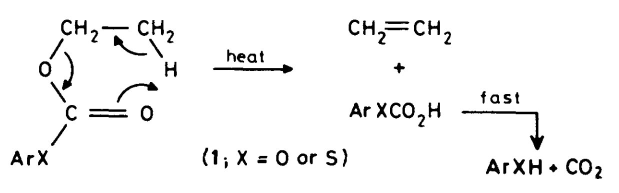
Rates of thermal decomposition of a range of *S*-aryl *O*-ethyl thiocarbonates have been measured over a 50 °C range for each compound, between 722.6 and 671.4 K. The compounds are less reactive than the corresponding aryl ethyl carbonates by a factor of *ca.* 2.0 at 679 K, owing to the smaller $-I$ effect of SAr relative to OAr. This provides further confirmation that the reactivity of esters towards thermal elimination parallels the extent of electron withdrawal by the group attached to the acyl carbon atom. The reaction gives a good Hammett correlation with σ° values, and ρ is 0.26 at 700 K, significantly greater than the value for the corresponding aryl ethyl carbonates. Thus sulphur is a better transmitter of electronic effects than is oxygen, and this transmission order, previously observed in studies in solution, is not a result of solvation phenomena. The *ortho*-methoxy substituent deactivates in thiocarbonate pyrolysis in contrast to its activation in carbonates. This probably arises from through-space $p_\pi \longrightarrow d_\pi$ bonding in the former compounds. An improved gold-plated stainless steel pyrolytic reactor is described.

The relative abilities of oxygen and sulphur to transmit electronic effects are of continuing interest, in particular in connection with the relative abilities of furan and thiophene to transmit substituent effects between the 2- and 5-position.[2] The results of studies in solution have been contradictory, though most indicate sulphur to be the better transmitter. Thus Marcus *et al.*[3] measured proton chemical shifts in XH or XCH_3 groups in substituted benzenes, where X is sulphur or oxygen, and found the latter to be the better transmitter. In contrast, the chemical shifts of the *trans*-β-hydrogen atoms in aryl vinyl ethers or sulphides,[4] the ^{13}C chemical shifts in the same compounds,[4] and the ionization constants of *cis*-β-phenoxyacrylic acids as compared with those for *cis*-β-phenylthioacrylic acids[4] all indicated sulphur to be the better transmitter; CNDO/2 calculations also confirmed that this should in general be true.[5] Since it is possible that the disagreement between the two sets of data reflects a solvation effect, we considered it useful to determine the relative transmission abilities in a gas-phase reaction.

Previously, Smith, Jones, and Taylor found that the rates of thermal decomposition of aryl ethyl carbonates (**1**; X = O) to ethene, carbon dioxide, and substituted phenol gave a good correlation with σ° values with $\rho = 0.19$ at 638 K (equivalent to 0.20 at 600 K).[6] (We have described[7] elsewhere the reason for requiring σ° values in these correlations, *e.g.* for benzoate[8] and *N*-arylcarbamate[7] pyrolysis). The stoicheiometry of the reaction is 3.0:1, owing to the very rapid secondary decomposition of the carbonic acid.

In order to determine the relative abilities of sulphur and oxygen to transmit electronic effects in the gas phase, we have prepared a series of the corresponding sulphur compounds (**1**; X = S) and measured their rates of thermal elimination. The Hammett ρ factor for a reaction is a function of both the ability of the system to transmit electronic effects and the amount of charge to be stabilized. Use of the ethyl compounds for both series ensures that the transition state polarities will be as nearly identical as possible.[9] This requirement of near identity means that the ArO and ArS groups should have close similar effects upon the reaction rate, which they do.



Results and Discussion

Each thiocarbonate gave excellent reproducible kinetic results, first-order to >98% reaction; the stoicheiometry was 3.0:1. The kinetic data (Table) gave excellent Arrhenius plots with no deviant points, as indicated by the correlation coefficients. In the experience of one of us (R.T.) this is much the most reliable indicator of the absence of surface-catalysed elimination (see also ref. 10). The relative rates at 700 K gave a satisfactory Hammett correlation (Figure) with σ° values, and the ρ factor is 0.26, equivalent to 0.30 at 600 K. This is significantly larger than the value of 0.20 for carbonates, and confirms that sulphur is a better transmitter of substituent effects than is oxygen. It seems probably therefore that the work indicating the

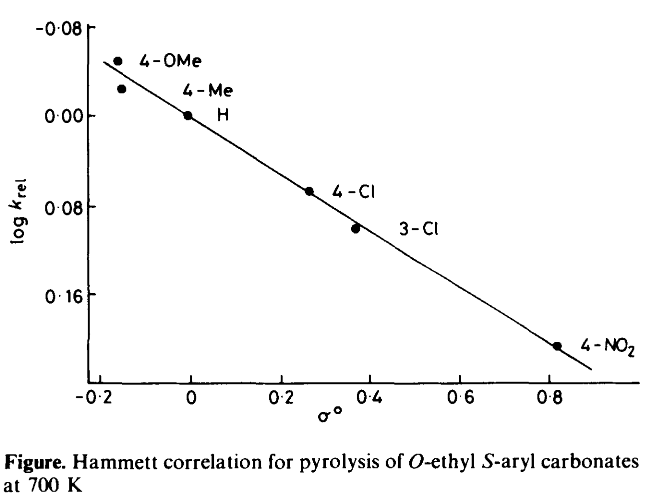


Figure. Hammett correlation for pyrolysis of *O*-ethyl *S*-aryl carbonates at 700 K

Table. Pyrolysis of *S*-aryl *O*-ethyl thiocarbonates ($XC_6H_4SCO_2Et$)

X	*T*/K	10^3 *k*/s^{-1}	*E*/kJ mol^{-1} [a]	log(*A*/s^{-1}) [b]	Corr. coefft.	10^3 *k*/s^{-1} (700 K)
H [c]	722.6	40.7	46.696	12.735	0.999 99	14.2
	705.7	18.6				
	690.7	9.09				
	671.4	3.40				
4-MeO	721.6	34.1	46.359	12.580	0.999 95	12.7
	706.2	17.2				
	690.5	8.07				
	671.4	3.05				
2-MeO	722.6	33.5	45.863	12.396	0.999 78	11.9
	705.7	15.2				
	690.7	7.86				
	671.4	2.89				
4-Me	721.6	36.8	47.009	12.808	0.999 97	13.5
	706.2	18.3				
	690.5	8.50				
	671.4	3.18				
4-Cl	722.6	45.3	45.729	12.491	0.999 98	16.3
	705.7	21.4				
	690.7	10.5				
	671.4	4.00				
3-Cl	721.6	48.1	45.191	12.366	0.999 53	18.0
	706.2	24.2				
	690.5	11.0				
	671.4	4.62				
4-NO_2	721.6	60.1	45.217	12.478	0.999 99	22.8
	705.7	29.8				
	690.7	14.8				
	671.4	5.69				

[a] ±0.5 kcal mol^{-1}. [b] ±0.2 s^{-1}. [c] At 679 K ethyl phenyl carbonate gave $k = 9.4 \times 10^{-3}$ s^{-1} (slightly less than the rate which may be calculated from the literature data,[11] owing to recalibrated thermocouples *etc.* used from Part 2 of this series onwards).

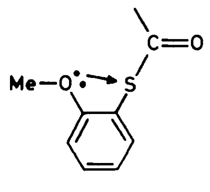
reverse order may have reflected an aspect of solvation which could in particular have affected the relative ionization of phenols and benzenethiols.

Relative Reactivities of Carbonates and Thiocarbonates.—The foregoing conclusion is based on the assumption that the transition states are of similar polarity. To confirm this we measured the rate for ethyl phenyl carbonate at 679 K; this is 1.86 times more reactive than the corresponding thiocarbonate. This accords with the general trend to which we have previously drawn attention,[11] namely that the reactivity of esters towards thermal elimination depends upon the extent of electron withdrawal (or supply) by the group attached to the acyl carbon atom. Reactions are therefore faster the greater the $-I$ effect of this group. (This factor for example makes carbonates more reactive than acetates, OR groups being more electron-withdrawing than R groups.) Since SAr is less electron-withdrawing than OR the observed results follows.

Similar values (but not exactly equal ones in view of the differing ρ factors) will apply to other pairs of carbonates and thiocarbonates, and consideration of the ρ factors for the reaction shows that ρ will be smaller the greater the electron-withdrawal in the aryl ring. Thus ρ is 2.02 for the 4-methoxy compounds but only 1.27 for the 4-nitro compounds. This is understandable of course, because the greater the electron withdrawal by the aryl ring, the less important the differential effect of oxygen and sulphur becomes. Conversely, when the electron withdrawal is reduced, as for example when Ar is replaced by alkyl groups, a greater difference in reactivity should be, and is, observed. Thus from the rates of pyrolysis of ethyl methyl carbonate[12] and *O*-ethyl *S*-methyl thiocarbonate,[13] the reactivity of the former to the latter may be calculated to be 4.40 at 679 K.

Effect of the 2-Methoxy Substituent.—In carbonate pyrolysis the 2-methoxy substituent activates slightly; this is understandable on the basis of the greater effectiveness of the $-I$ effect from the *ortho*-position. In contrast, in this thiocarbonate pyrolysis this substituent deactivates, an observation not explicable in terms of any through-bond electronic effects, even if the greater transmission ability of sulphur is taken into account.

We believe therefore that this result arises from through-space $p_\pi \longrightarrow d_\pi$ bonding [see (**2**)], which provides a mode of additional electron release to sulphur, not of course available in the carbonates. Through-space electronic effects have been manifest in previous studies of gas-phase eliminations.[14]



(**2**)

Experimental

Each of the thiocarbonates was made by cautious addition, with cooling, of pyridine (10 ml) to the appropriate benzenethiol (0.1 mol) and ethyl chloroformate (0.3 mol). The mixture was then heated during 1 h. Normal work-up and fractional distillation gave the thiocarbonates as follows: *O*-ethyl *S*-phenyl thiocarbonate (67%), b.p. 81—82 °C at 1.0 mmHg (lit.,[15] 69.5—70 °C at 0.3 mmHg); δ ($CDCl_3$) 7.60—7.80 (5 H, m, ArH), 4.27 (2 H, q, CH_2), and 1.28 (3 H, t, CH_3); *O-ethyl* S-(4-*methyl-*

phenyl) thiocarbonate (95%), b.p. 88 °C at 2.2 mmHg (Found: C, 61.3; H, 6.2. $C_{10}H_{12}O_2S$ requires C, 61.2; H, 6.1%); δ($CDCl_3$) 7.44 and 7.23 (4 H, dd, ArH), 4.28 (2 H, q, CH_2), 2.34 (3 H, s, ArCH_3), and 1.29 (3 H, t, CH_3); O-*ethyl* S-(4-*methoxyphenyl*) *thiocarbonate* (70%), b.p. 102 °C at 0.5 mmHg (Found: C, 56.6; H, 5.8. $C_{10}H_{12}O_3S$ requires C, 56.6; H, 5.7%); δ($CDCl_3$) 7.47 and 7.39 (4 H, dd, ArH), 4.27 (2 H, q, CH_2), 3.78 (3 H, s, OMe), and 1.29 (3 H, t, CH_3); O-*ethyl* S-(2-*methoxyphenyl*) *thiocarbonate* (73%), b.p. 82—83 °C at 0.2 mmHg (Found: C, 56.6; H, 5.7%); δ($CDCl_3$) 7.53—7.30 (2 H, m, ArH), 7.06—6.86 (2 H, m, ArH), 4.25 (2 H, q, CH_2), 3.83 (3 H, s, OMe), and 1.28 (3 H, t, CH_3); *O*-ethyl *S*-(4-chlorophenyl) thiocarbonate (62%), b.p. 78 °C at 1.2 mmHg (lit.,[16] b.p. 142—143 °C at 10 mmHg); δ($CDCl_3$) 7.50—7.25 (4 H, m, ArH), 4.24 (2 H, q, CH_2), and 1.30 (3 H, t, CH_3); O-*ethyl* S-(3-*chlorophenyl*) *thiocarbonate* (95%), b.p. 100 °C at 2.2 mmHg (Found: C, 50.0; H, 4.2. $C_9H_9ClO_2S$ requires C, 49.9; 4.2%); δ($CDCl_3$) 7.43 (1 H, s, ArH), 7.27 (3 H, m, ArH), 4.20 (2 H, q, CH_2), and 1.28 (3 H, t, CH_3); O-*ethyl* S-(4-*nitrophenyl*) *thiocarbonate* (65%), m.p. 75 °C [from light petroleum (b.p. 40—60 °C)] (Found: C, 47.6; H, 4.0; N, 6.4. $C_9H_9NO_4S$ requires C, 47.6; H, 4.0; N, 6.2%); δ($CDCl_3$) 8.23 and 7.71 (4 H, dd, ArH), 4.36 (2 H, q, CH_2), and 1.35 (3 H, t, CH_3).

Kinetic Studies.—The general method of carrying out the kinetic runs has been described,[17,18] but the present work was carried out with a new reactor incorporating a number of improvements over its predecessor, which developed metal fatigue after *ca.* 2 000 runs. Improvements were as follows.

(i) The interior surface was coated with Specpure (99.999%) gold (*i.e.* iridium-free) in order to diminish the incursion of surface-catalysed reactions. Good adhesion between this gold (which had to be vacuum deposited) and the stainless steel surface of the reactor was unobtainable. The interior surface of the latter was therefore electroplated with 99.5% gold, then the high purity gold was deposited upon this.

(ii) The distance between the pressure-sensitive diaphragm and the glass-to-metal seal (needed for carrying the electrical signal from the diaphragm at the body of the reactor) was increased by 10 cm. This displaced the seal (sealed into the stainless steel pressure-blancing tube with silver solder) further from the heat of the reactor, so increasing the life of the seal. This will permit the reactor to be used at higher temperature envisaged in projects in progress.

(iii) Connection between the electrical contact on the diaphragm and the glass-to-metal seal (copper in the original equipment[18] and gold in the improved version[17]) was made from platinum wire. The advantage (apart from stiffness, which facilitated threading the wire through the contact on the glass-to-metal seal during assembly) is that when this connection wire is soft-soldered to the glass-to-metal seal, an alloy is not produced as was the case with gold. The gold alloy was degraded with time, requiring more frequent servicing than is now the case. At the diaphragm contact end, the wire was spot-welded to the contact, thereby eliminating a further soldered connection.

(iv) Double O-ring seals were used on each of the two reactor valves. This improved vacuum quality and increased intervals between the need to replace the seals.

(v) The insulation at the valve end of the reactor (formerly Asbestolux) was replaced with Triton Kaowool Board 'strong' grade with additionally hardened surfaces (Morgan Ceramic Fibres Ltd.). Apart from being safer, this insulation has considerably lower thermal conductivity, necessary for the higher temperature work planned.

(vi) Gold wire was used for the connections between the platinum resistance thermometer and the A.E.I RT3R temperature controller. Copper was previously used, but oxidation caused long-term instability in temperature control. With this new set-up, at temperatures of the order of 450 °C no variation was detected (±0.05 °C sensitivity) during 7 days (the longest period tested at any one temperature).

Acknowledgements

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