Thermolytic Reactions of Esters. Part XI.† Vapour-phase Thermolysis of Allyl Methyl Oxalate and Allyl Phenyl Oxalate and its Relevance to the Thermochemistry of Oxycarbonyl Radicals

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The title compounds homolyse in the vapour phase (flow system: 400—500°). Of the intermediate $\cdot CO_2R$ radicals those with R = methyl or allyl decarboxylate whereas the phenyl analogue loses carbon monoxide. Thermochemical aspects are considered: it is concluded that the carbon dioxide and carbon monoxide formed in photolysis or thermolysis of liquid oxalates in the presence of iodine do not arise through decomposition of $\cdot CO_2R$ radicals.

RECENTLY we have shown that the vapour-phase thermolysis of diallyl oxalate,[1] a homolytic reaction, proceeded markedly faster than that of allyl acetate [2] or that of allyl benzoate.[3] A multiple scission [step (1)] was suggested as the first step, followed by decarboxylation (2) of the oxycarbonyl radical (II). If this interpretation is correct, variation of R would lead to (almost) identical rates of step (1). We have therefore studied the thermolysis of compounds (Ib) and (Ic).

Moreover, such a study could lead to a better insight into the (thermo)chemistry of oxycarbonyl radicals (II).

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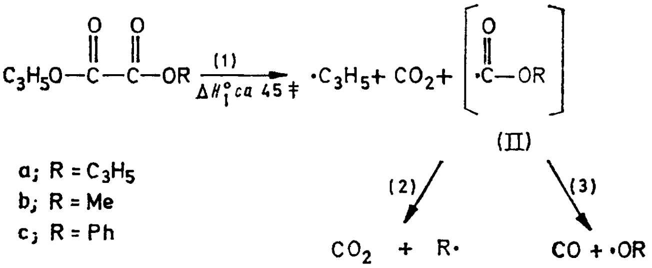
† Part X, P. C. Oele and R. Louw, *Tetrahedron Letters*, 1972, 5159.

[1] R. Louw, *Rec. Trav. chim.*, 1971, **90**, 469.

[2] R. Louw and E. C. Kooyman, *Rec. Trav. chim.*, 1965, **84**, 1511.

[3] R. Louw and E. C. Kooyman, *Rec. Trav. chim.*, 1967, **86**, 147.

Whereas recent work[4,5] strongly points to $k_2 \gg k_3$ for R = alkyl, others suggest a competitive breakdown in



‡ Energies are expressed in kcal mol⁻¹.

this case;[6] the fate of (IIc) has thus far only been subject to speculation.[6b]

RESULTS AND DISCUSSION

Thermolysis of Allyl Oxalates.—Employing our standard techniques[1,7] we have obtained the data outlined in Tables 1 and 2. It is seen that dimethyl oxalate (run 19, Table 1) is essentially stable under conditions where allyl oxalates show large degrees of conversion. This proves that mere breaking of the central C–C bond[8] is not involved in the thermolysis of (I). The product pattern (Table 2) substantiates the free radical nature of the latter type of reaction.

The thermal stabilities of (Ia—c) are seen to be equal within a factor of two, as expected for (1) being the rate-determining step.

Judging from $CO_2 : CO$ ratios, compound (Ib) follows steps (1), (2), and (4), as does (Ia),[1] with $k_2 > k_3$. Compound (Ic) however, appears to react mainly according to steps (1), (3), and (5), the phenol : benzene ratio, and hence k_3/k_2, being $> 80/0{\cdot}3 = ca.\ 270$ * [*cf.* Table 2, (Ic)–*m*-xylene experiments].

$$R\cdot + ArMe \longrightarrow RH + ArCH_2\cdot \qquad (4)$$
$$PhO\cdot + ArMe \longrightarrow PhOH + ArCH_2\cdot \qquad (5)$$

TABLE 1

Thermolysis of oxalates $C_3H_5(CO_2)_2R$ (I)

No.[a,b]	R	Temp. (°C)	Average residence time(s)	Conversion (%) [c]	Remarks
1	Me(Ib)	538	2·3	39 ± 2	*d*
2	Me(Ib)–C_3H_5(Ia) [e]	515	2·5	19/30	k_{1b}/k_{1a} 0·55
3	Me(Ib)–C_3H_5(Ia) [e]	528	2·4	28/51	k_{1b}/k_{1a} 0·38
4	Me(Ib)–C_3H_5(Ia) [e]	540	2·4	37/70	k_{1b}/k_{1a} 0·40
5 [f]	Me(Ib)	445	164	21	
6	Me(Ib)	456	171	25	
7	Me(Ib)	475	162	67	
8 [g]	Me(Ib)	475	184	69	
9	Me(Ib)	491	139	65	
10	Me(Ib)	490	156	65	
11	Me(Ib)	500	155	89	
12	Me(Ib)–C_3H_5(Ia) [e]	460	164	49/69	k_{1b}/k_{1a} 0·45
13	Me(Ib)–C_3H_5(Ia)	496	148	72/85	k_{1b}/k_{1a} 0·45
14 [f]	Ph(Ic)	410	170	*ca.* 5	
15	Ph(Ic)	460	146	40	
16 [g]	Ph(Ic)	465	174	58	
17	Ph(Ic)	485	169	75	
18	Ph(Ic)–C_3H_5(Ia) [e]	455	154	39/39	k_{1c}/k_{1a} *ca.* 1
19	Dimethyl oxalate	490	140	<1	*h*

[a] Experiments 1—4, microreactor–g.l.c. system; other runs in a macroreactor of *ca.* 750 ml capacity. [b] In a large excess of toluene and nitrogen (*ca.* 1 : 1), unless otherwise stated. [c] By g.l.c. analysis (*cf.* Experimental section). [d] Variation from 1—10·8 mole % of ester in toluene, the results showing the first-order nature of the thermolysis. [e] Competitive runs. [f] At 400°, the degrees of conversion of (Ib) and (Ic) were <4%. [g] In *m*-xylene rather than toluene. [h] <0·5% CO or CO_2 formed.

Thermochemistry.—There are very few data on gaseous heats of formation of oxalates. However, with the aid of recent values for ethyl oxalate[10] and phenyl oxalate[8] and using reliable group increment data † a consistent set (Table 3) is obtained. With D(C–C) = 70 for the central

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* It is supposed that Ph· and PhO· quantitatively react according to steps (4) and (5), respectively. The $k_3 : k_2$ ratio thus estimated has to be considered as a minimum, however. The very small amount of benzene [*ca.* 0·2% based on (Ic) consumed] is, in fact, not unlike that of toluene, apparently formed from *m*-xylene, in *ca.* 0·1% (based on xylene consumed). A homolytic mechanism, involving $H\cdot + ArZ \longrightarrow ArH + Z\cdot$ as a chain-propagating step,[9] can adequately explain these side reactions; from (Ic), Z· (= $\cdot OCO{-}OCOC_3H_5$) will subsequently decompose into $2CO_2$ + allyl·.

† For acetates $MeCO_2R$, ΔH_f^0 values are R = Me (−98);[11] Et (−106);[11] Ph (−67),[10] thus showing increments Me ⟶ Et (−8) and Et ⟶ Ph (+39). For the two oxalates[8,10] the latter value is 36·5. As a compromise we have taken 38. The increment Et ⟶ allyl is taken as +25, the value for aliphatic hydrocarbons.

[4] R. K. Solly and S. W. Benson, *Internat. J. Chem. Kinetics*, 1969, **1**, 427.

[5] (*a*) P. Cadman, A. J. White, and A. F. Trotman-Dickinson, *J.C.S. Faraday I*, 1972, 506; (*b*) D. Griller and B. P. Roberts, *J.C.S. Perkin II*, 1972, 747.

[6] (*a*) K. Bartel, A. Goosen, and A. Scheffer, *J. Chem. Soc.* (*C*), 1971, 3766; (*b*) A. Goosen and A. Scheffer, *J.C.S. Perkin I*, 1972, 369.

[7] A. Tinkelenberg, *J. Chromatog. Sci.*, 1970, **8**, 721.

[8] A. S. Carson, D. H. Fine, P. Gray, and P. G. Laye, *J. Chem. Soc.* (*B*), 1971, 1611.

[9] R. Louw and H. J. Lucas, *Rec. Trav. chim.*, 1973, **92**, 55.

[10] J. D. Cox and G. Pilcher, 'Thermochemistry of Organic and Organometallic Compounds,' Academic Press, New York, 1970.

[11] D. R. Stull, E. F. Westrum, jun., and G. C. Sinke, 'The Chemical Thermodynamics of Organic Compounds,' Wiley, New York, 1969.

bond in oxalates* standard heats of formation for oxycarbonyl radicals (·CO_2R) are then given In Table 4 (estimated uncertainties 2—3 kcal mol^{-1}). On this basis one derives ΔH_1^0 *ca.* 45,† in fair agreement with the rate data on allyl oxalate (Ia), log k_1 *ca.* 10·8 — 43/2·303RT.

TABLE 2

Survey of products[a]

(Ib), 2—5% in toluene	CO_2 (190 ± 10); CO (5—10); CH_4 (90 ± 10); A_2 (6—20); AB (30—60); B_2 (15—35) benzene (5—15)[b]
(Ib), in *m*-xylene	Benzene (<1); toluene (5—10)[c]
(Ic), 2—3% in toluene	CO_2 (*ca.* 100); CO (*ca.* 90); A_2 (5—10); AB (25—60); B_2 (*ca.* 25); phenol (80—100); benzene (5—15)[b]
(Ic), in *m*-xylene	Benzene (0·1—0·3); toluene (5—15)[c]

[a] Determined by g.l.c. (*cf.* Experimental section), given in mole % of converted ester: A_2 = biallyl, AB = 4-phenylbut-1-ene, B_2 = bibenzyl. [b] Produced from toluene, <0·2 mole %. [c] Produced from xylene, <0·2 mole %.

TABLE 3

Gaseous heats of formation for oxalates $R^1(CO_2)_2R^2$

R^1	R^2	Calculated (±1 kcal mol^{-1})	Experimental
Me	Me	−161	
Me	Et	−169	
Me	C_3H_5	−144	
Me	Ph	−131	
Et	Et		−177[a]
C_3H_5	C_3H_5	−127	
C_3H_5	Ph	−114	
Ph	Ph		−104[b]

[a] Ref. 10. [b] Ref. 8.

TABLE 4

Gaseous heats of formation for oxycarbonyl radicals ·CO_2R

R	ΔH_f^0	Other estimates
Me (IIb)	−45	−43;[a] −52[b]
Et (IIa)	−54	−57[b]
Allyl	−28	
Ph (IIc)	−17	−19 ± 5[b]

[a] Ref. 4 gives −40·4; however, these authors used ΔH_f^0-$(HCO_2Me)_g$ = −81, while ref. 10 gives −83·6. [b] Ref. 8.

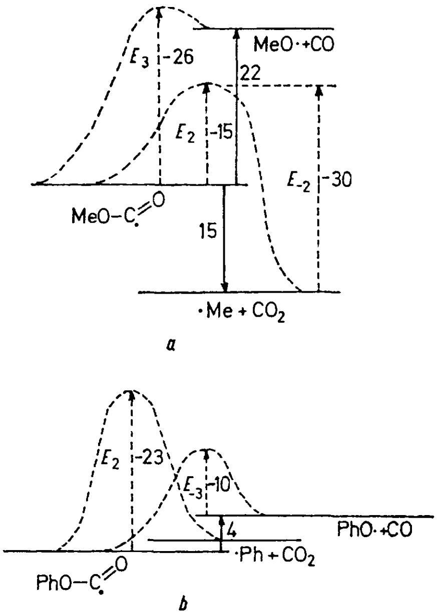
Thermal Decomposition of Oxycarbonyl Radicals.—From Table 5 it is seen that when heats of reaction are considered loss of CO_2 is highly preferred for the aliphatic radicals. Fragment (IIc) however, takes a different route. Although both decarboxylation and decarbonylation are almost thermoneutral, this radical in fact loses CO, with $k_3/k_2 \geqslant 10^{2\cdot4}$, suggesting a difference in activation energy of at least 8 kcal mol^{-1}. This preference can be understood on consideration of the Figure.

TABLE 5

Thermochemistry of decomposition of oxycarbonyl radicals by reactions (2) and (3)

R	$H_f^0(R\cdot)$ [12]	$H_f^0(RO\cdot)$ [12]	ΔH_2^0	ΔH_3^0	$\Delta H_3^0 - \Delta H_2^0$
Me (IIb)	34	3	−15	22	37
Et	26	−4	−14	24	38
Allyl (IIa)	40	23[a]	−26	25	51
Ph (IIc)	78[b]	13[c]	+1	+4	3

[a] From $H_f^0(EtO\cdot)$ = −4 and the CH_2 increment of −5 holding for hydrocarbons (and for corresponding ethers[11]), $H_f^0(Pr^nO\cdot)$ = −9; the increment for introduction of the double bond ($PrO \longrightarrow C_3H_5O$), +32, is an average value for some ethers[11] (*cf.* H_f^0 values: PrOPr −70; $C_3H_5OC_3H_5$ 0·8; PrOMe −56·8; C_3H_5OMe −25·5). [b] *Cf.* ref. 13. This value, corresponding to D(Ph–H) = 110, has also been found from studies of competitive gas-phase chlorination of benzene and chloroform.[14] [c] Value uncertain (±5 kcal mol^{-1} ?); *cf.* ref. 15.



Activation profile for decomposition of *a* MeOCO· and *b* PhOCO·

Figure *a*, the aliphatic case, has been drawn using E_2 = 15 (*cf.* E_2 = 13 for R = Pr^n [5]) and accepting E_{-3} = 4.‡

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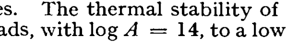
* From the well established ΔH_f^0 values for the molecules[10] and radicals,[12] D[MeC(O)–C(O)Me] = 67, D(Et–Et) = 82. In oxalates there may be somewhat less polar repulsion between the C atoms by virtue of resonance (i) than in corresponding α-diketones. As ·C(O)OR and ·C(O)R may have, at best, only a



$$\mathrm{RO{-}\overset{+}{C}{-}\overset{-}{O}} \longleftrightarrow \mathrm{R\overset{+}{O}{=}C{-}\overset{-}{O}} \qquad \text{(i)}$$

slight difference in radical stabilisation energy, we expect the central C–C bond to be a little stronger in oxalates than in analogous diketones. The thermal stability of dimethyl oxalate (Table 1, run 19) leads, with log A = 14, to a lower limit of 64 kcal mol^{-1} for the strength of the central bond.

† *E.g.*, (Ib) $\longrightarrow$ (IIb) + CO_2 + ·C_3H_5: ΔH_1^0 = 45, when using ΔH_f^0 = −144, −45, −94, and +40 for these species, respectively.

‡ This value holds for R· + CO (R = Me or CF_3);[16] ·Me and ·OMe also show comparable reactivities in hydrogen abstraction from alkanes.[17]

[12] S. W. Benson, 'Thermochemical Kinetics,' Wiley, New York, 1968.

[13] (*a*) G. A. Chamberlain and E. Whittle, *Trans. Faraday Soc.*, 1971, **67**, 2077; (*b*) T. Bérces, F. Márta, and I. Szilágyi, *J.C.S. Faraday I*, 1972, **68**, 867.

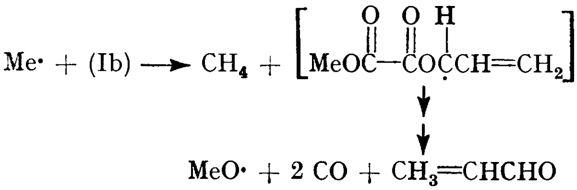
[14] (*a*) W. Dorrepaal, Thesis, Leiden, 1972; (*b*) W. Dorrepaal and R. Louw, in preparation.

[15] (*a*) D. H. Fine and J. B. Westmore, *Canad. J. Chem.*, 1970, **48**, 395; (*b*) R. Louw, *Rec. Trav. chim.*, 1971, **90**, 1119.

[16] J. A. Kerr and A. C. Lloyd, *Quart. Rev.*, 1968, **22**, 549.

[17] P. Gray, R. Shaw, and J. C. J. Thynne, *Progr. Reaction Kinetics*, 1967, **4**, 106.

Then, $E_3 - E_2 = ca.\ 11$, leading to $k_3/k_2 \leqslant 10^{-3}$ at 480°.*



$$\mathrm{Me\cdot} + \text{(Ib)} \longrightarrow \mathrm{CH_4} + \left[\mathrm{MeO}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}-\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{O}\overset{\overset{\mathrm{H}}{|}}{\underset{\cdot}{\mathrm{C}}}\mathrm{CH{=}CH_2}\right] \downarrow\downarrow \mathrm{MeO\cdot} + 2\,\mathrm{CO} + \mathrm{CH_3{=}CHCHO} \quad (6)$$

When going from R = Me to Ph one may expect that differences in bond dissociation energies lead to changes in activation barriers as well. Thus, the difference in Ph–OCO· and Me–OCO· bond strengths (*ca.* 16 kcal $\mathrm{mol^{-1}}$, *cf.* Table 5) may lead to E_2 *ca.* 23 rather than 15 (and to E_{-2} *ca.* 22 rather than 30) (Figure *b*). The resonance stabilisation of PhO·, implying a weaker PhO–CO· bond, will lead to a larger E_{-3} value. Assuming $E_{-3} = 10$ rather than 4, one arrives at $E_2 - E_3 = 9$ for R = Ph; tallying with the experimental facts.

For R = allyl (IIa) one may expect $E_{-3} = 4$ [as with (IIb)], but E_2 will now be $\leqslant 10$ rather than *ca.* 15. Hence $E_3 - E_2$ is expected to be at least 20, mainly as a consequence of the allylic resonance energy.

It is to be expected that the selectivities in the $\cdot\mathrm{CO_2R}$ thermolysis outlined above, *i.e.* $k_2 \gg k_3$ for R = alkyl or allyl and $k_2 \ll k_3$ for R = phenyl, also hold at lower temperatures (25—150°).

Goosen *et al.*[6] expressed different views, however. Although it is likely that $\cdot\mathrm{CO_2R}$ fragments were present in their liquid systems containing iodine, $\mathrm{CO_2}$ and CO (and hence RI and ROH) need not be formed *via* these intermediates. Especially it is unlikely that $\cdot\mathrm{CO_2R}$ loses CO at these temperatures (*cf.* E_3 *ca.* 26; Figure *a*); † the reaction $\cdot\mathrm{CO_2R} + \mathrm{I_2} \longrightarrow \mathrm{ICO_2R} + \mathrm{I\cdot}$, having little activation energy, will be a much faster process. We have outlined before [1] that the thermolysis of polar molecules, though homolytic in the vapour phase, may well involve a different (non-radical) mechanism in the liquid phase. When, in the latter case, polar reagents are present as well, a mechanistic analogy is certainly unwarranted. Thus, we suggest that the products, perhaps including the (mixed) oxalates, formed from hydrogen oxalates with $\mathrm{HgO{-}I_2}$ reagent [6a] are formed *via* $\mathrm{ICO_2R}$, presumably without involving free organic radicals.

EXPERIMENTAL

The apparatus and methods have been described elsewhere.[1,7]

Analyses.—The microreactor system was equipped with a Carbowax column (4m; 172°; He at 1·2 atm.). Retention times (in min) were biallyl 1·6, toluene 2·2, 4-phenylbut-1-ene 4·4, (Ib) 6·8, and (Ia) 11·6. Products from the macroreactor system were analysed as follows. (i) Volatile components (using the nitrogen carrier gas as internal standard): Porapak (25°; 0·8 atm.), $\mathrm{CH_4}$ and $\mathrm{CO_2}$; molecular sieves (120°; 0·8 atm.), CO and $\mathrm{CH_4}$. Calibration by means of synthetic mixtures led to conversion factors identical with those of Dietz.[20] (ii) Liquids: SE-30 and Ca-OV17, temperature and carrier gas pressures depending on the volatility of product.

Spectra.—N.m.r. spectra were taken with a Varian 60 MHz spectrometer, mass spectra with an AEI MS-902 apparatus.

Chemicals.—Nitrogen, toluene, and *m*-xylene were high-grade commercial products, checked by g.l.c. Biallyl (from allyl bromide and Mg in ether), 4-phenylbut-1-ene,[2] bibenzyl, and phenol were reference materials of sufficient purity. Diallyl oxalate (Ia) was from ref. 1. Allyl methyl oxalate (Ib) was made by addition of $\mathrm{ClCOCO_2Me}$ [21] (23·2 g, 19 mmol) to allyl alcohol–pyridine (19 mmol each) in $\mathrm{CH_2Cl_2}$ (50 ml) at 0°. After stirring (3 h) the pyridine hydrochloride was filtered off, the liquid washed with ice-water, and dried ($\mathrm{CaSO_4}$). Distillation afforded (Ib), b.p. 89—90° at 24 mmHg, n_{D}^{20} 1·4298 (16·2 g, 13·2 mmol, 70%). The n.m.r. and mass spectra supported the assigned structure. Allyl phenyl oxalate (Ic) was prepared by treatment of diphenyl oxalate (48 g, 0·2 mol; made according to ref. 22) with allyl alcohol (8·4 g, 0·14 mol) in benzene (18 g) and toluene-*p*-sulphonic acid (0·2 g). After warming at 90° for 1 h and standing overnight some $\mathrm{K_2CO_3}$ was added to the semisolid, benzene was removed *in vacuo*, and the crude product (Ic) was collected by vacuum distillation. Redistillation afforded pure material, b.p. 91° at 0·2 mmHg, $n_{\mathrm{D}}^{26\cdot5}$ 1·5068. The n.m.r. and mass spectra supported the assigned structure. Identical material, albeit in low yield, was obtained by treating oxalyl chloride with sodium phenolate (0·2 mol each) in dioxan, followed by allyl alcohol and pyridine (1 equiv. each) in $\mathrm{CH_2Cl_2}$ at room temperature. The filtrate was concentrated *in vacuo*, and the residue distilled. After mixtures of oxalic acid and compound (Ia) crude product (Ic) was obtained; redistillation afforded pure (Ic), b.p. 115° at 1·2 mmHg (2·5 g).

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* On this basis the carbon monoxide observed in the thermolysis of (Ib) (*cf.* Table 2) apparently arises in a different fashion. Most probably, part of the ·Me formed in reaction (2) reacts with (Ib) [reaction (6)] rather than with scavenger [reaction (4)], as was also outlined for allyl acetate thermolysis.[2] The MeO· fragments will decompose into H· and $\mathrm{CH_2O}$, the aldehyde being further converted to CO by free radical routes.[18] By g.l.c. (Porapak, 100°; SE-30, 65°) we have established that a little acrolein is, indeed, formed.

† The work of Zabel and Trahanovsky [19] on the thermolysis of the tritylazocarboxylate $\mathrm{Ph_3CN_2CO_2Me}$ in *e.g.* benzene shows that the $\cdot\mathrm{CO_2Me}$ radical is completely stable to decarboxylation at 60°.

[18] R. Klein, M. D. Scheer, and L. J. Schoen, *J. Amer. Chem. Soc.*, 1956, **78**, 50.

[19] D. E. Zabel and W. S. Trahanovsky, *J. Org. Chem.*, 1972, **37**, 2413.

[20] W. A. Dietz, *J. Gas Chromatography*, 1967, **5**, 68.

[21] P. L. Southwick and L. L. Seivard, *J. Amer. Chem. Soc.*, 1949, **71**, 2535.

[22] R. Adams and H. Gilman, *J. Amer. Chem. Soc.*, 1915, **37**, 2716.