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Enol Elimination Reactions. Part V.¹ A Study of the Mechanism of the Decarboxylative Elimination Reactions of Some Enol Sulphonates

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The rate constants for the fragmentation of a number of sulphonates, $Ar^{1}(Ar^{2}SO_{3})C=C(CO_{2}^{-})_{2}$, have been measured, and Hammett $\rho\sigma$ plots have been made from these measurements. The ρ^{+} value, for varying the aryl group Ar^{1} , is $-3\cdot1$, and the ρ value, for varying the aryl group Ar^{2} , is $+1\cdot17$. The values of m, ΔV^{1} , and the rate constants are discussed and compared with values derived for related compounds in the literature. The conclusion is drawn that the decarboxylative elimination is a more or less concerted fragmentation reaction in which a substantial build-up of positive charge on a vinyl carbon atom is achieved in the transition state.

WE have previously established the scope and limitations of the decarboxylative elimination reaction which follows the alkaline hydrolysis of the enol sulphonates (I).^{1,2} The acetylenic acid (4) is produced under exceptionally mild conditions by this reaction, but the success of the reaction is dependent upon the nature of the group R; in some cases the product isolated in place of the acetylenic acid (4) is the diacid corresponding to (2). In addition to the acidic products [(2) or (4)], and whatever the group R, the hydrolysis product (3) is always produced as well. The important reaction, then, is the decarboxylative elimination reaction (2) \longrightarrow (4).



The groups R which encourage elimination (Table 1, column 1) are those which would most easily support a carbonium ion at the carbon atom bearing the sulphonate group, and those groups which prevent elimination (Table 1, column 2) are those which would least tolerate such a carbonium ion.

There is thus a strong implication that, in the transition state, a high degree of positive charge is developed

¹ Part IV, I. Fleming and C. R. Owen, J. Chem. Soc. (C), 1971, in the press. at the carbon atom bearing the sulphonate group. At the time when this implication became clear, the



Successful and unsuccessful decarboxylative eliminations from compounds (1)

| | 1 () |
|---|---|
| Groups R for which the acetylenic product is observed | Groups R for which the acetylenic product is not observed |
| 2-Furyl 2-Thienyl ¢-MeO·C.H. | Me PhCH ₂ FtO C CH=CH |
| Ph Ph PhCH=CH MeCH=CH ⁻ | CCl ₃ PhCO |
| $ \begin{array}{c} \text{Me}[\text{CH=CH}]_2 \\ p \cdot O_2 \mathbf{N} \cdot C_6 \mathbf{H}_4 \\ m \cdot O_2 \mathbf{N} \cdot C_6 \mathbf{H}_4 \\ \end{array} $ | |
| $o - O_2 N \cdot C_6 H_4^{a}$ Cyclopropyl ^a | |

^a Only low yields of acetylenic acids were obtained in these cases.

development of positive charge at a vinyl carbon atom was unusual enough to justify further study. Since that time, the intermediacy of vinyl carbonium ions in

² I. Fleming and J. Harley-Mason, J. Chem. Soc., 1963, 4711 and 4778; E. J. D. Brown and J. Harley-Mason, J. Chem. Soc. (C), 1966, 1390; reviewed in J. Cymerman Craig, M. D. Bergenthal, I. Fleming, and J. Harley-Mason, Angew. Chem. Internat. Edn., 1969, 8, 429.

TABLE 2



Rates of reaction of compounds (6) in aqueous dioxan

| | | | | | Solvent | | |
|--|---|---------------------------------|--|--|------------------------|--------------|---|
| Αr β-C ₁₀ Η ₇ | X MeO Ph F H Cl Cl NO ₂ | Ү Н Н Н С І Н | $\begin{array}{c} k/s^{-1} \\ 3\cdot38 \times 10^{-2} \\ 1\cdot78 \times 10^{-3} \\ 5\cdot92 \times 10^{-4} \\ 1\cdot93 \times 10^{-4} \\ 1\cdot63 \times 10^{-4} \\ 6\cdot73 \times 10^{-5} \\ 6\cdot15 \times 10^{-6} \\ 3\cdot57 \times 10^{-7} \end{array}$ | рН 12·6 | [% dioxan (v/v)] 10 | T/°C 30∙0 | λ/nm ^a 238·4 238·9 240·5 239·5 242·0 238·0 238·7 240·5 |
| β-C ₁₀ H ₇ | н | н | $\begin{array}{c} 6\cdot 11	imes10^{-4}\ 1\cdot 91	imes10^{-3} \end{array}$ | 12.6 | 10 | 39∙0 47∙5 | 242.0 |
| β-C ₁₀ H ₇ | н | н | $\begin{array}{c} 1{\cdot}63 \times 10^{-4} \\ 1{\cdot}64 \times 10^{-4} \\ 1{\cdot}64 \times 10^{-4} \\ 1{\cdot}62 \times 10^{-4} \\ 1{\cdot}63 \times 10^{-4} \\ 1{\cdot}64 \times 10^{-4} \\ 1{\cdot}64 \times 10^{-4} \\ 1{\cdot}54 \times 10^{-4} \\ 1{\cdot}44 \times 10^{-4} \\ 1{\cdot}03 \times 10^{-4} \\ 6{\cdot}60 \times 10^{-5} \\ 1{\cdot}00 \times 10^{-5} \\ 1{\cdot}00 \times 10^{-6} \end{array}$ | $11.6 \\ 11.0 \\ 10.1 \\ 9.0 \\ 8.5 \\ 7.9 \\ 6.8 \\ 5.2 \\ 4.8 \\ 4.1 \\ 3.7 \\ 2.8 \\ 2.0$ | 10 | 30.0 | 242-0 |
| β-C ₁₀ H ₇ | Cl | Cl | $\begin{array}{c} 1{\cdot}54 \ \times \ 10^{-5} \text{d} \\ 8{\cdot}02 \ \times \ 10^{-6} \text{e} \\ 6{\cdot}53 \ \times \ 10^{-6} \text{e} \\ 6{\cdot}11 \ \times \ 10^{-6} \text{e} \\ 6{\cdot}17 \ \times \ 10^{-6} \text{e} \\ 6{\cdot}17 \ \times \ 10^{-6} \text{e} \end{array}$ | $ \begin{array}{r} 12 \cdot 6 \\ 11 \cdot 1 \\ 10 \cdot 3 \\ 9 \cdot 4 \\ 7 \cdot 8 \\ 7 \cdot 2 \end{array} $ | 10 | 30-0 | 238.7 |
| β-C ₁₀ H ₇ | NO_2 | Η | $\begin{array}{c} 1{\cdot}43 \times 10^{-5f} \\ 8{\cdot}91 \times 10^{-7} s \\ 4{\cdot}69 \times 10^{-7} h \\ 4{\cdot}27 \times 10^{-7} \\ 4{\cdot}09 \times 10^{-7} s \\ 3{\cdot}97 \times 10^{-7} s \end{array}$ | $ \begin{array}{r} 12 \cdot 6 \\ 11 \cdot 1 \\ 10 \cdot 3 \\ 9 \cdot 4 \\ 7 \cdot 8 \\ 7 \cdot 2 \end{array} $ | 10 | 30.0 | 240.5 |
| $\begin{array}{l} p 	ext{-} \mathrm{O}_2 \mathrm{N} \cdot \mathrm{C}_6 \mathrm{H}_4 \\ p 	ext{-} \mathrm{C}_{10} \mathrm{H}_7 \\ \mathrm{Ph} \\ p 	ext{-} \mathrm{MeC}_6 \mathrm{H}_4 \end{array}$ | Me | н | $\begin{array}{c} 1\cdot 26 \times 10^{-2} \\ 1\cdot 78 \times 10^{-3} \\ 1\cdot 58 \times 10^{-3} \\ 9\cdot 83 \times 10^{-4} \end{array}$ | 11.0 | 10 | 30.0 | $261 \cdot 0$ $238 \cdot 9$ $261 \cdot 5$ $261 \cdot 0$ |
| p-MeC ₆ H ₄ | MeO | н | $egin{array}{llllllllllllllllllllllllllllllllllll$ | 11.0 | 20 40 70 | 30.0 | 259.0 |
| Ph | Ме | н | $1.33 	imes 10^{-3} \ 1.08 	imes 10^{-3} \ 7.50 	imes 10^{-4}$ | 11.0 | 20 40 70 | 30.0 | 261.5 |
| β-C ₁₀ H ₇ | Me | н | $8\cdot47~	imes~10^{-4}$ | 11.0 | 70 | 30.0 | 238.9 |
| β-C ₁₀ H ₇ | MeO | н | $1\cdot13$ $	imes$ 10^{-2} | 11.0 | 70 | 30.0 | 238.4 |
| \mathbf{Ph} | MeO | н | $8{\cdot}40$ $	imes$ 10 ⁻³ | 11.0 | 70 | 30.0 | 258.5 |

^a The wavelength at which the reaction was followed. ^b The rate of elimination only, between pH 7·2 and 9·4, calculated from the data given as described in the text. ^c The rate of elimination only, between pH 7·2 and 11·1, calculated from the data given as described in the text. ^d 32% Ketone, 68% acetylenic acid. ^e 100% Acetylenic acid. ^f 92% Ketone, 8% acetylenic acid. ^g 59% Ketone, 41% acetylenic acid. ^h 24% Ketone, 76% acetylenic acid. ^f 18% Ketone, 82% acetylenic acid. ^f 12% Ketone, 88% acetylenic acid. ^k 11% Ketone, 89% acetylenic acid.

the solvolysis of vinyl halides ³⁻⁶ and vinyl sulphonates ^{7,8} and in deamination reactions ⁹ has been observed by many people.¹⁰ In most cases, considerable assistance to the formation of such ions is needed in the form of good leaving groups and helpful α -substituents such as phenyl or cyclopropyl. Our reaction (2) \longrightarrow (4) could involve such a vinyl carbonium ion, but it could also, as we originally suggested,¹¹ be a concerted elimination. We decided to investigate the extent to which, in the transition state, positive charge is accumulated at the carbon atom bearing the sulphonate group. This is an ideal situation for use of a Hammett plot. ester hydrolysis involved in the reactions of compound (1), and they can be followed spectrophotometrically.

The rate constants which we have measured are collected in Table 2. The parameters which we derived from these rates are collected in Table 3. On the pH-rate profile of the reaction of compound (6a), the rate is constant from pH 12.6 down to pH 7; it falls off smoothly below this pH, becoming very small below about pH 3. The pK_a values of the acid corresponding to (6a) in aqueous dioxan were measured, as were the pK_a values of benzylidenemalonic acid. The pK_a values of the latter compound in water could also be

TABLE 3

| Reaction | parameters | derived | from | the | data | of | Table 2 | |
|-----------|------------|---------|------|-----|------|----|----------|--|
| ittaction | parameters | ucrivcu | nom | | uara | O1 | I abic # | |

| Conditions | Compound | Parameter | Value |
|--|---|---|---|
| 10% Dioxan-water at 30° and pH 7 | (6; Ar = β -C ₁₀ H ₇ , changing X and Y) | ۶ ⁺ <i>a</i> | 3.12 ± 0.2 (r 0.997) |
| 10% Dioxan-water at 30° and pH 12.6 | (6, $X = Me$, $Y = H$, changing Ar) | ۶ ^ь | 1.16 ± 0.03 (r 0.999) |
| 10% Dioxan-water at pH $12{\cdot}6$ at $30{\cdot}0^\circ,$ at $39{\cdot}0^\circ$ and $47{\cdot}5^\circ$ | (6, $X = Y = H$, Ar = β -C ₁₀ H ₇) | $\Delta H^{\ddagger} \Delta S^{\ddagger}$ | 26·4 kcal mol ⁻¹ +9·2 e.u. |
| 10% Dioxan–water to 70% dioxan–water at 30° and pH 11·1 | (6, $X = MeO, Y = H$, Ar = p -MeC ₆ H ₄) | m ° | 0.14 |
| 10% Dioxan-water to 70% dioxan-water at 30° and pH 11.1 | (6, $X = Me$, $Y = H$, Ar = Ph) | mc | 0.09 |
| 10% Dioxan-water at 25° and pH 12.6 | (6, $X = Y = H$, Ar = β -C ₁₀ H ₇) | $\Delta V^{\ddagger a}$ | $+10.1 \pm 1 \text{ cm}^3 \text{ mol}^{-1}$ |

^a Plotted against σ^+ (H. C. Brown and Y. Okamoto, J. Amer. Chem. Soc., 1958, **80**, 4980). ^b Plotted against σ (H. C. Brown and Y. Okamoto, J. Amer. Chem. Soc., 1958, **80**, 4980). ^c As defined in E. Grunwald and S. Winstein, J. Amer. Chem. Soc., 1948, **70**, 846, using values for Y from A. H. Fainberg and S. Winstein, J. Amer. Chem. Soc., 1956, **78**, 2770. ^d Measured by Professor W. J. le Noble, University of New York at Stony Brook.

RESULTS

The synthesis of the diacids (5) is described elsewhere.¹ When the free acid (5) was dissolved in aqueous alkali, the elimination from the dianion (6) was



found to be clean; no competing substitution of the kind $(1) \longrightarrow (3)$ was observed and the acetylenic acids (7) were obtained in quantitative yield. Furthermore, the kinetics of the reaction are uncomplicated by the

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 ⁴ L. L. Miller and D. A. Kaufman, *J. Amer. Chem. Soc.*, 1968, 90, 7282.

measured; this enabled us to make a rough estimate that the pK_a values of the acid corresponding to (6a) in 10% dioxan in water, our usual reaction medium, would be about 2.5 and 4.6. These measurements are not reliable enough for us to be able to say whether the monoanion is just as reactive as, or whether it is much less reactive than, the dianion (6a). We do note, however, in all our measurements, that the first and second pK_a values of these benzylidenemalonic acids are much closer to each other than is normal with malonic acids.

DISCUSSION

The Anomalous Cases of Compounds (6b) and (6c).— One troublesome aspect of the rate data was an anomalously high rate for both the 3,4-dichloro-compound (6b) and the p-nitro-compound (6c). As originally measured at the pH (12.6) used for all the other compounds they gave rates which were too high (by factors of 2.5 and 40,

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¹¹ I. Fleming and J. Harley-Mason, Proc. Chem. Soc., 1961, 245.

⁵ Z. Rappoport and A. Gal, J. Amer. Chem. Soc., 1969, 91, 5246.

⁶ Z. Rappoport and Y. Apeloig, J. Amer. Chem. Soc., 1969, 91, 6734; S. A. Sherrod and R. G. Bergman, *ibid.*, p. 2115; M. Hanack and T. Bässler, *ibid.*, p. 2117; D. R. Kelsey and R. G. Bergman, *ibid.*, 1970, 92, 228; C. A. Grob and R. Spaar, *Tetrahedron Letters*, 1969, 1439; Z. Rappoport and A. Gal, *ibid.*, 1970, 3233; S. J. Huang and M. V. Lessard, J. Amer. Chem. Soc., 1968, 90, 2432.

^{90, 2432.} ⁷ Z. Rappoport and J. Kaspi, J. Amer. Chem. Soc., 1970, 92, 3220.

⁸ P. E. Peterson and J. M. Indelicato, J. Amer. Chem. Soc., 1969, 91, 6194; W. M. Jones and D. D. Maness, *ibid.*, 1970, 92, 5457; P. J. Stang and R. Summerville, *ibid.*, 1969, 91, 4600; G. Capozzi, G. Melloni, G. Modena, and U. Tonellato, Chem. Comm., 1969, 1520.
⁹ W. M. Jones and F. W. Miller, J. Amer. Chem. Soc., 1967,

respectively) to fit on the Hammett plot. As it happens, the solvolyses of benzyl chlorides and benzyl tosylates also show this upward drift with substituents having high σ values.¹² However, in our case, the unusually high rate is not due to a change of mechanism. We eventually found that the 3,4-dichloro- and the p-nitrocompounds, unlike the unsubstituted compound (6a), showed a rate which was dependent upon pH at pH values above 7. Furthermore, the reaction was no longer simple: the ketones (8a) and (8b) were produced, together with the acetylenic acids.

(8)
COMe a;
$$X = Y = Cl$$

b; $X = NO_2$, $Y = H$

When the reaction was run at lower pH, the production of ketones (8) dropped, and the rate dropped too. This reduction in the rate levelled off at about pH 10 for the dichloro-compound and at about pH 8 for the p-nitrocompound. In the case of the dichloro-compound the ketone (8a) was only found in reactions above pH 11, but in that of the p-nitro-compound it was still present, to the extent of about 11 per cent, even at pH 7. The ketones (8) are primary products and are not produced from the acetylenic acids (7), which are stable under the reaction conditions. If we multiply the rates of decomposition of (6b) and (6c) by the fraction of acetylenic acid in the product mixture, we get a measure of the rate of the elimination reaction itself. This rate (Table 4) is independent of pH up to pH 11, but there appears to be an increase in the rate at pH 12.6. When the rates of elimination for (6b) and (6c) in the pHindependent region are used in the Hammet plot in place of the overall rates of decomposition, they now fit in well with the points derived for the other compounds in the series.

The small rate increase in the elimination reaction at the highest pH is somewhat surprising. Similar observations were made in a study 13 of the decarboxylative dehydrobromination of the cinnamic acid dibromide (9). A reaction, first-order in hydroxide ion (dehydro-



bromination), was observed at high pH, but the rate of decarboxylative dehydrobromination was also increased. This increase was ascribed to hydroxide ion attack on the carboxylate ion. We are sceptical of this explanation but it is difficult to reject it simply on the basis that there is only one well established case 14 of attack by an anionic nucleophile on a carboxylate ion.

We can account for the formation of the ketones (8)with more assurance. The formation of ketone (8b), the rate of which we have been able to measure at three different hydroxide ion concentrations (Table 4), is



Rates of elimination and substitution of compounds (6b) and (6c) in 10% dioxan-water at 30°

| | | | | Ketone | | |
|-----------------|--------------|---------------|-----------------------------|-----------|------------------------------|-------------------------------|
| х | \mathbf{Y} | \mathbf{pH} | k/s-1 | (%) | $k_{\rm elim.}/{\rm s}^{-1}$ | $k_{\rm subst.}/{\rm s}^{-1}$ |
| Cl | Cl | 12.6 | $1.54	imes10^{-5}$ | 32 | $1.05	imes10^{-5}$ | $4.93 	imes 10^{-6}$ |
| | | 11.1 | 8.02×10^{-6} | 0 | $8\cdot02	imes10^{-6}$ | |
| | | 10.3 | $6.53	imes10^{-6}$ | 0 | $6\cdot 53	imes10^{-6}$ | |
| | | 9.4 | $6 \cdot 11 \times 10^{-6}$ | 0 | $6\cdot 11 	imes 10^{-6}$ | |
| | | 7.8 | 6.17×10^{-6} | 0 | $6\cdot 17 	imes 10^{-6}$ | |
| | | $7 \cdot 2$ | 6.17×10^{-6} | 0 | $6\cdot 17 	imes 10^{-6}$ | |
| NO ₂ | н | 12.6 | $1{\cdot}43	imes10^{-5}$ | 92 | 1.10×10^{-6} | 1.32×10^{-5} |
| - | | 11.1 | $8.91 	imes 10^{-7}$ | 59 | $3\cdot 63 	imes 10^{-7}$ | $5\cdot28$ $	imes$ 10^{-7} |
| | | 10.3 | $4.69 	imes 10^{-7}$ | 24 | $3\cdot 58 \times 10^{-7}$ | 1.11×10^{-7} |
| | | 9 ∙4 | $4.27 	imes 10^{-7}$ | 18 | $3\cdot51$ $	imes$ 10^{-7} | $7.60	imes10^{-8}$ |
| | | 7.8 | 4.09×10^{-7} | 12 | $3\cdot 62 	imes 10^{-7}$ | 4.70×10^{-8} |
| | | $7 \cdot 2$ | 3.97×10^{-7} | 11 | $3\cdot 53 	imes 10^{-7}$ | 4.44×10^{-8} |

first-order in hydroxide ion concentration. Since the ketones are not formed from the acetylenic acids, there are only two likely paths. One path is hydroxide-ion attack at the conjugate position, on the vinyl carbon atom; this is analogous to the formation of the ketone (3) from the sulphonate (1), except that attack is now on a dianion instead of on a neutral molecule, and that in the intermediate anion charge is delocalised on to the ionised carboxylate groups. Such attack is likely to be as difficult as the attack of hydroxide ion directly on a carboxylate ion. A second path is hydroxide-ion attack on the sulphonate groups. Two cases in the literature give us an estimate for the rate of such a reaction: the alkaline hydrolyses of cholest-2-en-3-yl toluene-p-sulphonate 15 and of phenyl toluene-p-sulphonate.¹⁶ The rate constant for the former is $3.17 \times$ 10^{-4} l mol⁻¹ s⁻¹ at 56° in 50% methanol (if it is assumed that the hydrolysis is first-order in hydroxide ion), and the second-order rate constant for the latter is 1×10^{-5}

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 ¹⁴ A. F. Hegarty and T. C. Bruice, *J. Amer. Chem. Soc.*, 1970,

^{92, 4924.} ¹⁵ N. Frydman, R. Bixon, M. Sprecher, and Y. Mazur, *Chem.*

Comm., 1969, 1044. ¹⁶ C. A. Bunton and V. A. Welch, J. Chem. Soc., 1956, 3240.

 $1 \ {\rm mol^{-1}} \ {\rm s^{-1}}$ at 30° in 70% dioxan. We find that the second-order rate constant for the formation of ketone (8b) is $3.3 \times 10^{-4} \,\mathrm{l}\,\mathrm{mol}^{-1}\,\mathrm{s}^{-1}$ at 30° in 10% dioxan-water. Even if these rates were corrected to allow for differences in temperature and solvent they would not be very different from each other. This mechanism is therefore reasonable for the formation of the ketones from those compounds whose rates of decarboxylative elimination are very low.

The decarboxylative elimination reaction (6) \longrightarrow (7). Having settled the matter of the two anamalous points in our Hammett plot, we now have an excellent 17 fit with σ^+ values covering a wide range, from which we derive a ρ^+ value of $-3\cdot 1$. This is a high negative value and confirms our original supposition that the carbon atom bearing the sulphonate group develops a high degree of positive charge in the transition state. We must now consider whether this charge grows to a full positive charge, giving a vinyl cation as an intermediate. We can consider three extreme mechanisms as possible.



Mechanism (I) has k_1 as a rate-determining step with k_2 rapid relative to k_{-1} . Mechanism (II) has k_2 slow relative to k_{-1} ; in other words, there is a readily reversible pre-equilibrium ionisation to give species (10), followed by slow decarboxylation. Because no products other than the acetylenic acid are observed, the recombination of the ions (10) to give back compounds (6) does not have to compete with the capture of other nucleophiles; the intermediate (10) in either of these mechanisms would have to be an ion pair into which solvent does not intrude. (The reaction in methanol, for example, is as clean as it is in water; there was no sign of any methyl ethers). Mechanism (III) is a concerted decarboxylative elimination without the formation of an intermediate.

We can rule out mechanism (I) on several grounds. With this mechanism, the overall rate is determined by the rate of the ionisation (6) \longrightarrow (10). In the first place, the effect of change of solvent is too small. The m value we have measured is close to 0.1, whereas m values for ionisations are usually much higher. Thus α -phenylethyl chloride on solvolysis has ¹⁸ an *m* value of 1.2 and (a closer analogy) the vinyl sulphonate (11a) has ⁷ an m value of 0.4. Secondly, we can compare our rates with those for the ionisation of compound (11a). By extrapolating our rates to the conditions used for this compound we find that the rate constant for (6; X = OMe, Y = H, $Ar = p - MeC_6H_4$ would be 0.9 s⁻¹,

which is 10⁴ times greater than that measured ⁷ for (11a; Ar = p-MeC₆H₄) (8·1 × 10⁻⁵ s⁻¹). Thirdly, the ρ^+ value we measure is not as high as we might expect from analogies in the literature. For example, the protonation of phenylpropiolic acids 19 gives a p+ value of -4.77; the protonation of phenylacetylene, 20 -3.84; the ionisation of triphenylvinyl iodide, 4 - 3.6; and, in the closest analogy, the ρ^+ value we calculate from the data⁷ given for the two compounds (11a) and (11b) is



-3.6. This value was obtained at 75° and would, no doubt, be larger (negative) at 30° , the temperature we have used. The difference in solvents is probably not responsible for the difference in the ρ^+ values: when the sulphonates (6; X = MeO and Me, Y = H, $Ar = \beta$ - $C_{10}H_7$) reacted in 70% dioxan, the difference in rates corresponded to a ρ^+ value of -2.4 (cf. -2.75 for these two points in 10% dioxan, and -3.1 for all points in 10% dioxan). Finally, the volume of activation, ΔV^{\ddagger} , is +10 cm³ mol⁻¹, a value much too high for a rate-determining ionisation step, which would be expected ²¹ to have a fairly high negative volume of activation, in the region of -15 cm³ mol⁻¹.

In mechanism (II) both the pre-equilibrium, measured by k_1/k_{-1} , and the rate of decarboxylation, measured by k_2 , contribute to the overall rate. The effect of solvent on these two steps will be in opposite directions: k_1/k_{-1} would be increased, and k_2 would be decreased, by a polar solvent. Similarly the ρ^+ value would be high and negative for the pre-equilibrium, but should be positive for the second step. The value we find, -3.1, would be the compromise value. Similarly the ΔV^{\ddagger} value may be a compromise between the negative value for an ionisation step and a positive value which would be expected as the consequence of the charge neutralisation in the second step.

One decarboxylative elimination reaction, the fragmentation of β -bromoangelate ion,²² gave a high ΔV^{\ddagger} value $(+17.7 \text{ cm}^3 \text{ mol}^{-1})$ which can be expected to be the minimum value for a perfectly concerted elimination. If, in the transition state for a concerted reaction [mechanism (III)], the carbon-sulphonate bond is more stretched than the carbon-carboxylate bond, there will be an uneven charge distribution which may benefit from solvation more than the transition state for a

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&</sup>lt;sup>21</sup> W. J. le Noble, Progr. Phys. Org. Chem., 1967, 5, 207; E. Whalley, Adv. Phys. Org. Chem., 1964, 2, 93.
²² W. J. le Noble, R. Goiten, and A. Shurpik, Tetrahedron

Letters, 1969, 895.

more perfectly synchronised fragmentation. The maximum value of ΔV^{\ddagger} would not be observed, but rather some lower value. Moreover the value of ρ^+ may be quite high in such circumstances. We have therefore to distinguish between mechanism (II) and mechanism (III) by other criteria.

The first criterion, which supports mechanism (III), is a comparison of our rates with the rates of reaction of several related compounds reported in the literature. These are collected in Table 5, where they are corrected

TABLE 5

Comparison of the rates of decomposition of the compounds $p-XC_6H_4$ ·CBr=CR¹R² (R² cis to Br) in 80% ethanol at 70°

| Entry | х | R1 | \mathbb{R}^2 | k/s-1 | ΔH^{\ddagger} | ΔS^{\ddagger} | Ref. |
|----------|--------------|---------------|-------------------|---------------------------------|-----------------------|-----------------------|-----------|
| 1 | н | \mathbf{H} | н | $6 \times 10^{-11} a$ | $34 \cdot 1$ | -7.8 | 3 |
| 2 | н | \mathbf{Ph} | \mathbf{Ph} | $2	imes 10^{-9}$ b | 26 | -5 | 7 |
| 3 | H | н | CO_2^- | $7	imes10^{-8}$ ° | 27.6 | -13.3 | 25 |
| 4 | \mathbf{H} | CO2- | H | $1	imes10^{-8}$ d | 41.2 | +30.5 | 25 |
| 5 | н | CO_2 | CO_2^- | $2	imes 10^{	ext{-4}	extsf{b}}$ | 26.4 | +9.2 | This |
| | | | | | | | work |
| 6 | MeO | н | н | $2	imes 10^{-6}$ a | | | 3 |
| 7 | MeO | \mathbf{Ph} | \mathbf{Ph} | $6	imes10^{-6}$ | | | 5 |
| 8 | MeO | \mathbf{H} | CO ₂ - | $5	imes 10^{-5}$ ° | | | 25 |
| 9 | MeO | CO2- | CO_2^- | $5	imes 10^{-2}$ b | | | This |
| | | - | | | | | work |

" These values are lower limits for the rate of ionisation. The rate measured may actually be the rate of ionsation. The rate measured may actually be the rate of the reaction initiated by protonation, see W. B. Schubert and G. W. Barfknecht, J. Amer. Chem. Soc., 1970, **92**, 207. But see also Z. Rappoport, T. Bässler, and M. Hanack, J. Amer. Chem. Soc., 1970, **92**, 4985. ^b Using $k_{\rm OTs}/k_{\rm Br} = 32$. ^c Using m =0.2. ^d Using m = 0.3.

to correspond to a common leaving group (the bromide ion), temperature, and solvent, and are, consequently, no more than approximate. In converting our rates to the rate for a bromide leaving group, we have used the factor 32 for $k_{\rm OTs}/k_{\rm Br}$, which is the value observed by Rappoport⁷ for tris-*p*-methoxyphenylvinyl tosylate and bromide. Our reaction probably has a smaller value than this, and our rates, entries 5 and 9 in Table 5, would then be larger, if anything. Table 5 shows that our compounds react considerably faster than the triarylvinyl system, entries 2 and 7, where the ratedetermining step is ionisation. The effect of a substituent β to the leaving group is known ⁷ to be small. It is true that the carboxylate ion may assist the solvation of the developing positive charge but it is unlikely to do so to any greater extent than that found in saturated systems, where the effect is small 23,24 (usually a factor less than 100) whether the carboxylate ion is participating as a nucleophile²³ or not.²⁴ The most likely explanation for our rates being so noticeably higher than those of the triarylvinyl systems is that the carboxylate group is beginning to become detached in the transition state.

²³ C. A. Kingsbury, J. Org. Chem., 1968, 33, 3247.
²⁴ F. G. Bordwell and A. C. Knipe, J. Org. Chem., 1970, 35, 2959, and references therein.

25 C. A. Grob, J. Csapilla, and G. Cseh, Helv. Chim. Acta, 1964,

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It can also be seen that Grob's decarboxylative dehydrobrominations ²⁵ (entries 3, 4, and 8) go considerably faster than the simple ionisation of styryl bromides³ (entries 1 and 6), and, what is more, they go faster for both the cis- and the trans-isomers. The presence of a carboxylate ion near, but not involved in, the solvolysis of alkyl bromides is known²⁴ to cause rate enhancements of up to 280-fold over the rate for the simple alkyl bromide. Thus Grob ascribes 25 the rate increase in the trans-cinnamic acid (entry 3) to charge neutralisation of the developing positive charge by the carboxylate ion cis to the leaving group, but in the cis-cinnamic acid (entry 4) he ascribes the much greater rate to concerted decarboxylative elimination. Our rate appears to show the sum of these effects, in that we have carboxylate groups both *cis* and *trans* to the leaving group and have an even greater rate of reaction. In Grob's compounds, the entropy of activation for the transcinnamic acid (entry 3) is -13.3, and for the *cis*-cinnamic acid (entry 4) it is +30.5. The high positive value in the latter case is at least partly a result of the formation of three fragments in the rate-determining step; the negative value in the former case implies that the fragmentation is not concerted for the trans-cinnamic acid. Our entropy of activation is not as large as Grob's but is still positive, the lower value being, perhaps, the result of the contribution of the cis-carboxylate group, whatever that may be.

The second criterion, which also supports mechanism (III), is the p value for the leaving group. It is surprising to find that ρ values for varying an arenesulphonate group have only rarely been measured: people are usually happy to use a brosylate-to-tosylate ratio of 3 (which corresponds to a ρ value of 1.2). The few measured ρ values are, it is true, fairly close to 1.2. For example, in the hydrolysis of ethyl arenesulphonates 26 in 30% ethanol at 25°, it is 1.168, and in that 27 of methyl are nesulphonates in 50% ethanol at $50\degree$, it is 1.248. The ρ value can be a little higher than this; the hydrolysis ²⁷ of isopropyl arenesulphonates in 50% ethanol at 25° gives a ρ value of 1.565, and the highest we know of, 1.67, is that for the hydrolysis ⁷ of tris-pmethoxyphenylvinyl arenesulphonates (11a) in 70% acetone. In contrast with the latter, our ρ value, 1.16, is one of the lowest ever observed. The relatively low ρ values for primary sulphonates probably reflects a high degree of solvent participation in the ionisation process. The larger value for the vinyl sulphonates probably reflects the absence of such assistance as well as the difficulty in generating vinyl cations. In view of the recent work ²⁸ on secondary arenesulphonates, it will be interesting to see if the p value of adamant-2-yl arenesulphonates is higher than those for cyclohexyl and isopropyl arenesulphonates.

27 R. E. Robertson, Canad. J. Chem., 1953, 31, 589, with p

⁴⁷, 1590. ²⁶ L. Demény, *Rec. Trav. chim.*, 1931, **50**, 60, with p calculated by Jaffé in ref. 17.

 ²⁸ J. L. Fry, J. M. Harris, R. C. Bingham, and P. von R. Schleyer, J. Amer. Chem. Soc., 1970, 92, 2540; P. von R. Schleyer, J. L. Fry, L. K. M. Lam, and C. J. Lancelot, *ibid.*, p. 2540 2542.

The low value for ρ which we observe for the leaving group, contrasting with the high ρ value for the tris-pmethoxyphenylvinyl arenesulphonates, is not what would be expected for mechanism (II). In that mechanism, the leaving group will affect only the equilibrium step and not the decarboxylation step. There is no obvious reason why the p value for the pre-equilibrium should be lower than that for ionisation—the preequilibrium will be very endothermic and the transition state for ionisation will resemble the ion-pair product of this step; thus any factors affecting the ionisation should affect the pre-equilibrium similarly. The contrast in the ρ values is again made greater by the fact that the ρ value for the ionisation of tris-p-methoxyphenylvinyl arenesulphonates was measured at 75°, whereas ours was measured at 30°. That the difference in solvent is not responsible for the low value in our case was checked by taking the rates of the arenesulphonates (6; X = Me, Y = H, $Ar = \beta - C_{10}H_7$ or Ph) in 70% dioxan: the ρ value for these two points was 1.1 and had obviously not increased strikingly as a result of the change of solvent. The value in 70% dioxan with a *p*-methoxy-substituent (6; X = MeO, Y = H, $Ar = \beta$ -C₁₀H₇, Ph, or p-MeC₆H₄) was also about 1.2. Thus, the fragmentation mechanism, mechanism (III) in which the loss of CO₂ assists the ionisation of the sulphonate group, explains both the high rate constants of our compounds compared to those of the model compounds in Table 5, and also the relatively low o value for the leaving group.

In conclusion, we have established that our decarboxylative enol elimination reaction is a more or less concerted fragmentation, in which a substantial positive charge is built up on the vinyl carbon atom bearing the sulphonate group. We note that, whereas the decarboxylative elimination reaction of our compounds (6) is concerted, the decarboxylative elimination reaction of (9), with a poorer leaving group but in the saturated series, is both faster and, in water, proceeds by ratedetermining ionisation.^{13,24} This difference in mechanism is probably at least partly a reflection of the difficulty of generating vinyl cations, but it may also be simply a reflection of the factors, such as conformational rigidity and the greater ease of bond breaking to the electrofugal leaving group, which cause concerted elimination to give acetylenes to be faster than concerted elimination to give olefins.29

We can now see why the yields of some of the acetylenic acids we have observed in the past (Table 1) were low—the reaction had gone nowhere near to completion in the overnight treatment which was then the customary procedure. We can now also place a more definitive limit on the kinds of group R in (1) for which acetylenic acid formation can be expected to occur: the group R must be at least as good as a p-nitrophenyl group in supporting positive charge on an adjacent carbon atom. If the group R is equal to or worse than p-nitrophenyl in this capacity, the rate of decarboxylative elimination is so slow that hydrolysis of the sulphonate ester intercedes.

EXPERIMENTAL

Kinetics .-- The rate constants were measured by the following general procedure. The diacid (5) (4 mg) was dissolved in dioxan (20 ml). This solution (1 ml) was added to the aqueous buffer solution (9 ml) to make a solution which was 0.1M in buffer and which contained enough potassium chloride to make it of unit ionic strength. The rates were followed to three half-lives on a Zeiss PMQ 11 at the wavelength (given in Table 2) which is an absorption minimum in the solution of the products when the leaving group is naphthalene- β -sulphonate, but is a maximum in all the other cases. The buffers used were: pH 12.6 and 11.6, trifluoroethanol-sodium hydroxide; 11.0 and 10.1, sodium hydrogen carbonate-sodium carbonate; 9.0 and 8.5, 'tris'-hydrochloric acid; 7.9 and 6.8, sodium dihydrogen phosphate-disodium hydrogen phosphate; 5.2, 4.8, and 4.1, acetic acid-sodium acetate; 3.7 and 2.8, formic acid-sodium formate; 2.0, hydrochloric acid. The pH values of these buffers were measured with a Vibron electrometer 33B.

The pK_a values were calculated from titration curves taken by J. A. Radley (Laboratories) Ltd., Reading.

The Ketonic Products.—In the cases of compounds (6b) and (6c) the kinetics were followed by the procedure just described, but the product mixtures were analysed from runs which were comparable in every respect except that the concentrations of the diacids were 0.02M (instead of 0.00005M) and a larger total volume of solution (50 ml) was used. The reaction mixture was acidified with hydrochloric acid and extracted with ether (6×80 ml); the extract was dried (Na₂SO₄) and then treated with an excess of diazomethane solution (20 ml). The ether was distilled off *in vacuo*, the residue was taken up in carbon tetrachloride, and the proportions of the acetylenic ester and ketone products were estimated from the n.m.r. spectrum.

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²⁹ S. I. Miller, J. Org. Chem., 1961, 26, 2619.

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