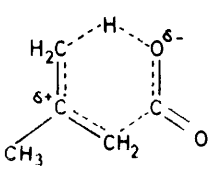
Studies in Decarboxylation. Part 15.[1] The Effect of 3-Substitution on the Rate of Decarboxylation of βγ-Unsaturated Acids

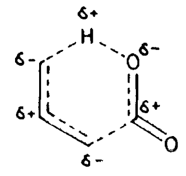
By **Amal Al-Borno** and **David B. Bigley,*** University Chemical Laboratory, Canterbury, Kent CT2 7NH

The kinetic effect of substituents at C(3) of βγ-unsaturated acids is consistent with the development of a partial positive charge at that position during decarboxylation. The OMe group increases the rate of decarboxylation as much as 10^5—10^6 fold.

THE gas-phase decarboxylation of βγ-unsaturated acids has been firmly established as a concerted unimolecular process.[2] We recently proposed[3] that there is a polar component in the reaction which could be represented in the dipolar transition state (I). Shortly afterwards Dewar and Ford[4] reported results of MINDO/3 calculations in agreement with (I), but adding the detail shown in (II). The calculations implied the development of a sizeable positive charge at C(3).[4]



(I)

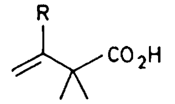


(II)

We have undertaken an experimental test of the charge distribution in the transition state and report below our results for C(3); part of these have appeared in preliminary form.[5]

RESULTS AND DISCUSSION

The Table shows a series (III)—(VI) of α-geminal dimethylated but-3-enoic acids which have differing substituents R at C(3); the choice of substituent was somewhat limited by the synthesis of the acid. The kinetics of pyrolysis of these acids were measured in our flow machine;[6] all had kinetics of the first order, were unaffected by pressure, by addition of radical traps, and by change of surface : volume ratio. The reactions are therefore unimolecular. The first two columns of the Table show the experimental data, and indicate that the usual 1,5-hydrogen shift in a cyclic concerted transition state occurs with these acids; the reaction products are those expected from this mechanism.[7]



(III) $R = H$
(IV) $R = CH_3$
(V) $R = CF_3$
(VI) $R = Cl$

The third column of the Table shows a ' best ' value for $\Delta H^{\ddagger}$, which is calculated from the experimental $\Delta G^{\ddagger}$, and the established mean value of $\Delta S^{\ddagger}$ for this transition state is -43.5 J K^{-1} mol^{-1}.[8] It is these values which are used to calculate the rates of column 4.

Comparison of acids (III)[9] and (IV)[9] was what led us to propose the dipolar transition state under examination.[3] These acids need no further discussion and are included only for comparison.

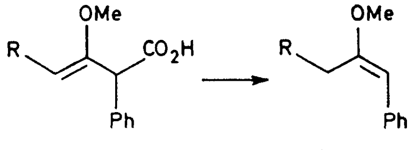
Inclusion of the electron-withdrawing trifluoromethyl group in acid (V) reduces the rate of decarboxylation about seven-fold in comparison with (III). This is clearly consistent with the development of some positive charge in the transition state at C(3), destabilized by the $-I$ interaction.

Arrhenius parameters, first-order rate constants and relative rates for the gas-phase decarboxylation of acids (III)—(VI) at 576.5 K

Acid	$\Delta H^{\ddagger}$/ kJ mol^{-1}	$\Delta S^{\ddagger}$/ J K^{-1} mol^{-1}	' Best ' $\Delta H^{\ddagger}$/ kJ mol^{-1}	10^3k/ s^{-1}	Relative rate
(III)[9]	149 ± 6	−44.4 ± 10	150	0.97	1
(IV)[9]	134 ± 6	−49.8 ± 10	138	12.0	12
(V)	157 ± 6	−47.3 ± 10	159	0.14	0.14
(VI)	148 ± 8	−29.9 ± 12	140	8.2	8.4

The $-I$ effect of a chlorine atom normally slightly outweights its $+M$ effect[10] (*e.g.* electrophilic attack on either vinyl chloride or chlorobenzene). The seven-fold increase in rate resulting from the introduction of the chlorine atom in 3-chloro-2,2-dimethylbut-3-enoic acid (VI) could therefore imply development of a partial negative charge at C(3) during decarboxylation. Alternatively the normal near balance between $-I$ and $+M$ may be altered for interaction with a fractional charge.

For this reason we chose the methoxy-group as a substituent; here it is certain that the $+M$ will outweigh the $-I$ effect.[10] Unfortunately, simple 3-methoxybut-3-enoic acids are not recorded in the literature, but 3-methoxy-2-phenylpent-3-enoic acid (VII; R = Me) had been reported to melt with decarboxylation at 82—83 °C.[11] It is therefore too thermally unstable for investigation in the gas phase and it was examined in solution. For comparison to be made between the two phases it is necessary to show that the decomposition in solution involves the normal concerted 1,5-shift. The following observations require this to be so.



(VII) (VIII)

(i) The product of decarboxylation, 2-methoxy-1-phenylbut-1-ene (VIII; R = Me), showed the double bond isomerisation characteristic of this mechanism.[7] On the other hand the unchanged acid showed no isomerisation to the αβ-unsaturated form.

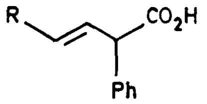
(ii) The reaction was of the first order in α-methylnaphthalene solution in the temperature range 360—381 K. The activation parameters are: $\Delta H^{\ddagger}$ 109 kJ mol^{-1}, $\Delta S^{\ddagger}$ −17 J K^{-1} mol^{-1} at 365 K. Significant errors are to be expected in these values as they are derived from measurements over only 21 K; nevertheless $\Delta S^{\ddagger}$ is firmly negative in value, indicating a cyclic transition state.

(iii) $k_H/k_D = 2.5$ in α-methylnaphthalene solution at 365 K, showing that the O–H bond is breaking in the transition state.

(iv) The rate of reaction was the same in α-methylnaphthalene and nitrobenzene solutions. These two solvents have very different polarities; the identity of the rates shows that ions are not formed in the reaction.

Collectively this evidence requires that the decarboxylation of (VII; R = Me) in solution proceeds by the concerted 1,5-hydrogen shift typical of the gas-phase decomposition of βγ-unsaturated acids.[2] As the rates of concerted reactions are not solvent dependent, the solution data may be compared directly with gas-phase data.

The effect of the 3-methoxy-group in this system would be most directly deduced by comparing the rate of decarboxylation of the methoxy-acid (VII; R = Me) with its unsubstituted counterpart (IX; R = Me). Although this acid was not available, 2-phenylbut-3-enoic acid (IX; R = H) served as a good model, and had k 2.5 × 10^{-3} s^{-1} at 309.9 °C. A γ-methyl group reduces the rate of decarboxylation of βγ-unsaturated acids about ten-fold,[9] and accordingly 2-phenylpent-3-enoic acid (IX; R = CH_3) may be expected to have k *ca.* 2.5 × 10^{-4} s^{-1} at 309.9 °C. Extrapolated to this temperature 3-methoxy-2-phenylpent-3-enoic acid (VII; R = CH_3) has k *ca.* 380 s^{-1}. The increase in rate associated with introduction of the 3-methoxy-group is therefore *ca.* 10^5—10^6-fold. Extrapolation of rate data over 200 K is likely to give rise to considerable error, but the calculated rate ratio is so large as to leave no doubt as to the dramatic accelerating effect of the methoxy-group.

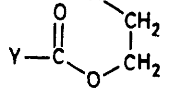


(IX)

A more direct comparison might have been made between 2-phenylbut-3-enoic acid (IX; R = H) and 3-methoxy-2-phenybut-3-enoic acid (VII; R = H). However, although the ethyl ester of the latter acid was successfully synthesised, all attempts at its hydrolysis resulted in concomitant decarboxylation to give 1-phenylpropan-2-one (the enol ether underwent hydrolysis). Presumably without the stabilizing γ-methyl group[9] the acid is not stable above room temperature.

Substitution of a methoxy-group on the α-position of ethyl chloride enhances its rate of pyrolysis by a factor of 10^7 at 603 K[12] or 10^9 at 500 K.[13] Extrapolation to 0° shows that pyrolysis and solvolysis continue to mirror each other in rate enhancement.[14] This is *ca.* 10^2 greater than the effect here described for acids, but comparison of polarity in the reactions is complicated by the different nature (four- *versus* six-centre) of the transition states.

In summary, all the substituents described here either require, or are consistent with, the development of positive charge at C(3) of the transition state for the decarboxylation of βγ-unsaturated acids. Although this transition state may not be as polar as that for halide pyrolysis, it is much more polar than that for acetate pyrolysis (X; Y = Me) where similar substitution of a methoxy-group to give carbonates (X; Y = OMe) results in only a 24-fold increase in rate of reaction.[15]



(X)

EXPERIMENTAL

3-Chloro-2,2-dimethylbut-3-enoic Acid (VI).—PCl_5 (104 g) was added to ethyl 2,2-dimethylacetoacetate[16] (32 g) at 0 °C and the mixture was kept at room temperature for one day. The mixture was then diluted with water (750 ml) and heated on a water-bath for 15 min. The chloro-ester was isolated with ether and after distillation was refluxed with 12% KOH in methanol (3 h) to give, after work-up, *3-chloro-2,2-dimethylbut-3-enoic acid* (VI), m.p. 54—55 °C (Found: C, 48.6; H, 6.1. $C_6H_9ClO_2$ requires C, 48.5; H, 6.1%).

2,2-Dimethyl-3-trifluoromethylbut-3-enoic Acid (V).—To a solution of ethyl 2,2-dimethyl-3-hydroxy-3-trifluoromethylbutanoate (18 g; from a Reformatskii reaction between 1,1,1-trifluoroacetone and ethyl α-bromoisobutyrate[9]) in benzene (50 ml) was added PBr_5 (45 g) and the mixture refluxed for 48 h. After standard work-up, hydrolysis with 10% methanolic KOH gave the *acid* as an oil, b.p. 60 °C at 0.3 mmHg (Found: C, 45.9; H, 5.0. $C_7H_9F_3O_2$ requires C, 46.2; H, 5.0%).

3-Methoxy-2-phenylpent-3-enoic acid had m.p. 82—83 °C (lit.,[11] 81—82 °C).

2-Phenylbut-3-enoic acid had m.p. 22—23 °C (lit.,[17] 23—24 °C).

Stoicheiometry.—All acids gave 100 ± 2% yield of CO_2. The yield of the organic product was not measured; in each case it was shown to be a single compound on two g.l.c. columns and to have the expected ^{1}H n.m.r. spectrum.

Kinetics.—The Arrhenius parameters for acids (V) and (VI) were obtained with our flow apparatus.[6] 2-Phenylbut-3-enoic acid was examined in a stainless steel static reactor,[18] while CO_2 evolution from acid (VII; R = Me) was followed with a gas burette.

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