Dramatic Acceleration of a Concerted Reaction by a Methoxy Group

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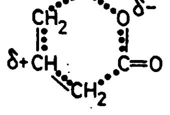
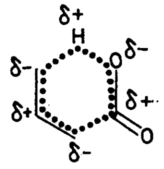
Summary The 10^5–10^6-fold increase of rate resulting from substitution by a methoxy group confirms the polarity of transition state in the decarboxylation of $\beta\gamma$-unsaturated acids.

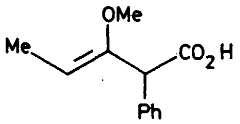
WE recently suggested[1] that the transition state for the thermal decarboxylation of $\beta\gamma$-unsaturated acids is concerted but of *dipolar* character (I) and that the hydrogen atom is transferred with protonic character. Very recently Dewar and Ford reported the results of MINDO/3 calculations which were in agreement with (I) but added the finer detail shown in (II)[2] and stated "the calculations imply development of a sizable positive charge at C(3). They also bear out the 'intuitive' transition state (II) in predicting development of negative charge at C(2) and C(4)".[2]



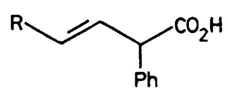
(I)



(II)



(III)



(IV)

In support of these conclusions we now report a dramatic increase in the rate of decarboxylation when the $+M$ methoxy group is attached to C(3).

3-Methoxy-2-phenylpent-3-enoic acid (III) has been reported to melt with decarboxylation at 82·3 °C.[3] It is therefore too thermally unstable for examination in the gas phase in direct comparison with our earlier work,[1] but the following evidence requires the same concerted mechanism for its decarboxylation.

(i) The product of decarboxylation, 1-phenyl-2-methoxybut-1-ene, shows the double bond shift characteristic of this mechanism.[4]

(ii) The reaction is of the first order and there is a loss of entropy on going to the transition state ($E_a = 106{\cdot}2$ kJ mol^{-1}, $\log A = 12{\cdot}1$).

(iii) The rate is the same in α-methylnaphthalene and in nitrobenzene solutions.

(iv) $k_H/k_D = 2{\cdot}5_5$.

2-Phenylbut-3-enoic acid (IV; R=H) has $k = 2{\cdot}5 \times 10^{-3}\ s^{-1}$ at 309·9 °C; extrapolated to this temperature (III) has $k = ca.\ 380\ s^{-1}$. For direct comparison it would have been desirable to examine 2-phenylpent-3-enoic acid (IV; R=Me), but this acid was not available. However, a γ-methyl group reduces the rate of decarboxylation about ten-fold,[5] and the latter acid should have $k = ca.\ 2{\cdot}5 \times 10^{-4}$ s^{-1} at the same temperature.

The rate enhancement resulting from substitution of a methoxy group at C(3) is therefore in the region of 10^5–10^6, lending strong support to the proposed positive charge development.

Methoxy groups have been observed to lead to large rate enhancements in other gas phase reactions in recent years,[6] but to date they have been associated with the formation of radicals and not with a concerted mechanism.

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[1] D. B. Bigley and R. H. Weatherhead, *J.C.S. Perkin II*, 1977, 592.

[2] M. J. S. Dewar and G. P. Ford, *J. Amer. Chem. Soc.*, 1977, **99**, 8343.

[3] O. Dimroth and H. Fenchta, *Ber.*, 1903, **36**, 2238.

[4] D. B. Bigley, *J. Chem. Soc.*, 1964, 3897.

[5] D. B. Bigley and R. W. May, *J. Chem. Soc.* (*B*), 1967, 557; D. B. Bigley and R. H. Weatherhead, *J.C.S. Perkin II*, 1976, 592.

[6] W. Kirmse and H. R. Murawski, *J.C.S. Chem. Comm.*, 1978, 392, and references cited therein.