Studies in Decarboxylation. Part 16.[1] Steric Inhibition of Resonance in a 1,5-Sigmatropic Reaction

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The rates of gas-phase decarboxylation of some 3-phenyl-substituted but-3-enoic acids are best rationalized in terms of steric inhibition of resonance in the more sterically crowded members.

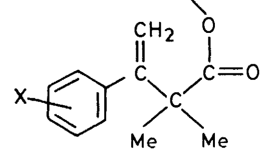
Some years ago we reported on the decarboxylation of a series of 2,2-dimethyl-3-phenylbut-3-enoic acids (I). Varying X from *p*-methoxy to *m*-nitro decreased the rate 26-fold, giving $\rho = -1.2$.[2] In solution the maximum value for ρ is >6,[3] so that even allowing for the elevated temperature of the decarboxylation reaction, only a small positive charge development at C(3) was implied. However, it was noted that steric hindrance between the *gem*-dimethyl group and the benzene ring might result in rotation of the benzene ring, reducing the effectiveness of overlap between the aromatic and olefinic π-systems. In such a case there could be much larger development of charge at C(3) than deduced from the observed ρ, obscured by inefficient transmission of the electronic influence of substituents; in effect the σ-values of the substituents would have been artificially reduced, and with them the apparent value of ρ. Support for this view came from a comparison of the u.v. spectra of the acids and their product alkenes.[2] However, Taylor has dismissed this suggestion as a consequence of his inspection of molecular models.[4]

We recently confirmed that there is indeed positive charge development at C(3) during decarboxylation [5] and MINDO 3 calculations showed it to be ' sizeable.' [6] The observation that positioning a methoxy group at C(3) increases the rate of decarboxylation 10^5—10^6-fold [1] shows experimentally that the charge at C(3) is indeed sizeable, and lends some support to our thesis involving steric inhibition of resonance. We felt it of interest to return to this problem and report its resolution below.

Discussion

Table 1 shows the rates and relative rates of decarboxylation of some 3-substituted but-3-enoic acids. The last three are the original acids discussed in Part 6 of this Series; [2] acids (II)—(VI) are compared at the same temperature.

It was originally argued that substitution of a phenyl group on to the 3-position of 2,2-dimethylbut-3-enoic acid [(VI) ⟶ (I), X = H] did not show the full potential of the phenyl group as a substituent; interaction between the *gem*-dimethyl group at C(2) and the phenyl group resulted in steric inhibition of resonance. The enhancement in rate of decarboxylation was *ca.* 125-fold. By contrast, substitution of the same group in the parent acid (II), giving the less hindered 3-phenylbut-3-enoic acid (IV), results in a 4 000-fold increase in rate of decomposition. The effect of a *p*-methoxy group is similarly attenuated in the α-dimethylated series. Thus, while the *p*-MeO group [in (V)] enhances the rate of decarboxylation 123-fold over that of its parent (IV), the same group only increases the rate about eight-fold in the hindered series [(I), X = *p*-MeO *versus* X = H].

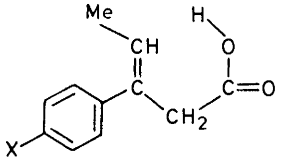


(I)

Table 1. Rates and relative rates of gas-phase decarboxylation of some 3-substituted but-3-enoic acids at 460.3 K

Acid	3-Substituent	2-Substituent	k/s^{-1}	Relative rate
(II) [7]	H		1.5×10^{-7}	1
(III)	p-NO_2–C_6H_4 [a]		2.0×10^{-4}	1 333
(IV)	C_6H_5		6.0×10^{-4}	4 000
(V)	p-MeO–C_6H_4 [a]		7.3×10^{-2}	490 000
(VI) [8]	H	Me_2	4.0×10^{-7}	2.7 (1)
(I) [2]	m-NO_2–C_6H_4	Me_2	1.5×10^{-5}	100 (37)
(I) [2]	C_6H_5	Me_2	5.1×10^{-5}	340 (130)
(I) [2]	p-MeO–C_6H_4	Me_2	39×10^{-5}	2 600 (960)

[a] Rate calculated assuming $\Delta S^\ddagger = -43.5$ J K^{-1} mol^{-1} (see Experimental section)

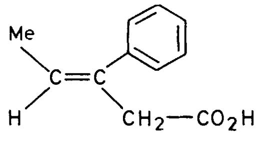


(VII) X = H
(VIII) X = OMe

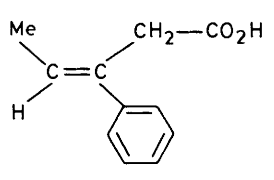
The rate-retarding effect of a nitro group is almost identical in the two series, even though it is a *para*-substituent in one case (III) and *meta*- in the other (I). The nitro group can only exert its inductive effect on C(3), being unable to interact conjugatively with an incipient carbonium ion. Since inductive effects are largely transmitted *via* sigma bonds the angle subtended by the phenyl group to the carbonium ion centre is not important and both series may be expected to be affected similarly.

These various rate ratios are thus easily accommodated by the assumption that the acids of the type (I) have their phenyl groups at an angle to the plane of the alkene and that the effects are thereby diminished; there does not seem to be another reasonable rationale.

We have also examined 3-phenyl- (VII) and 3-*p*-methoxyphenyl-pent-3-enoic (VIII) acids. At 542.9 K they have for (VII), $k = 5.4 \times 10^{-4}$, and for (VIII), $k = 9.2 \times 10^{-3}$ s^{-1}. It was possible only to compare these acids at this single temperature. Below this temperature acid (VIII) was not sufficiently volatile for use in the static reactor; above 542.9 K its rate of reaction was too fast. The rate ratio for (VIII): (VII) is 17.1; if



(VII)-*Z*



(VII)-*E*

$\Delta S^‡$ is assumed and the rates are calculated at 460.3 K, as in Table 1, the ratio becomes 28 : 1. The rates so calculated are extrapolated over 80 °C and cannot be usefully compared with the individual rates of Table 1. Pent-3-enoic acid has been examined previously in the range 680—720 K,[9] and the activation parameters give $k_{542.9} = 5.3 \times 10^{-6}\ \text{s}^{-1}$; once again the large extrapolation of temperature makes the precise numbers unreliable, but this is *ca.* 100-times slower than the 3-phenyl-substituted acid. The 3-phenylpent-3-enoic acids are therefore intermediate between the two series of Table 1 in their kinetic behaviour, implying some degree of steric hindrance. The *Z*-form of the acid, (VII)-*Z*, has interaction between the methyl and phenyl groups. The resulting rotation of the latter will reduce both its own effectiveness and that of a *p*-methoxy substituent, as found. The *E*-form [(VII)-*E*] has no such interaction but, in comparison with *trans*-pent-3-enoic acid, the approach of the carboxyl to C(4) during decarboxylation will be hindered by the methyl group. This should reduce the rates of the phenyl and the *p*-methoxyphenyl acids equally. We could not establish the stereochemistry of our acids independently, but their kinetic behaviour suggests that they are in the *Z*-form.

Experimental

The experimental data below are more limited than would be desired. Sometimes this was a consequence of experimental difficulty in the synthesis of the acid; the very small quantity permitted only one duplicate rate measurement. In other cases unfavourable combinations of volatility and reactivity limited the range of kinetic measurement. An example is shown in Table 2; all the pressure–time curves fitted well the first-order rate expression, giving the rate constants of the middle column. However, there is a doubling of volume during the reaction; therefore $P_0 = 0.5P_\infty$ and the lower ratios recorded for the two lower temperatures of Table 2 are attributed to incomplete volatility at the beginning of the reaction. It was felt advisable to disregard these points. In order to adjust the rate constants from the Experimental section to the single temperature of Table 1 the 'standard' $\Delta S^‡$ for the decarboxylation reaction ($-43.5\ \text{J K}^{-1}\ \text{mol}^{-1}$)[10] has been assumed. This procedure is not ideal, but the temperature adjustments are quite small and the resultant errors in the rate constants will not be large.

All the acids described below except 3-*p*-nitrophenylbut-3-enoic acid gave 100 ± 3% of CO_2 and the expected[11] alkene as sole products of decarboxylation. With the same exception, unchanged acids recovered from partial reaction contained no isomeric material.

3-*Phenylbut*-3-*enoic Acid* (IV).—Prepared by the method of Maercker and Weber,[12] this had m.p. 49—49.5 °C (lit.,[12] 48—49.5 °C).

3-p-*Nitrophenylbut*-3-*enoic Acid* (III).—Prepared by reaction between the Reformatskii reagent from ethyl bromoacetate and *p*-nitroacetophenone, the hydroxy-ester dehydrated spontaneously on distillation (140—142 °C at 1 mmHg) and the resulting unsaturated esters were hydrolysed with 5% aqueous KOH. The desired acid was then separated from its isomer *via* the basic copper salt[13] and had m.p. 124—125 °C (from CCl_4), mol. wt. 207.

Table 2. Rate constants for the pyrolysis of 3-phenylbut-3-enoic acid

T/K	$10^3\ k/\text{s}^{-1}$	P_0/P_∞
443.1	0.8	0.25
453.1	1.1	0.33
473.1	1.8	0.5
493.1	4.2	0.5

3-p-*Methoxyphenylbut*-3-*enoic Acid* (V).—This was prepared in the same way as the previous acid except that the hydroxy-ester was dehydrated by a 0.5 h reflux with $POCl_3$ in benzene. It was recrystallized from light petroleum (b.p. 60—80 °C), m.p. 99—100 °C (Found: C, 68.7; H, 6.3. $C_{11}H_{12}O_3$ requires C, 68.8; H, 6.3%.)

3-*Phenylpent*-3-*enoic Acid* (VII).—This was prepared from a Grignard reaction between t-butyl bromoacetate[14] and propiophenone, the synthesis being completed according to Johnson and Kon.[15] It had b.p. 130 °C at 0.1 mmHg (lit.,[15] 152.9 °C at 26 mmHg).

3-p-*Methoxyphenylpent*-3-*enoic Acid* (VI).—This was prepared from *p*-methoxypropiophenone in the same manner as acid (III) and recrystallized from light petroleum (b.p. 40—60 °C), m.p. 72—73 °C (Found: C, 69.9; H, 6.7. $C_{12}H_{14}O_3$ requires C, 69.9; H, 6.8%.)

All the acids and their product alkenes had the expected ^{1}H n.m.r. spectra.

Kinetics.—The kinetics were measured in either a stainless-steel static reactor[7] (A) or evacuated breakseal tubes (B): (II) (A) see Table 2; (III) (B) underwent isomerization ($k = 2.3 \times 10^{-4}\ \text{s}^{-1}$) and decarboxylation ($k = 2.1 \times 10^{-4}\ \text{s}^{-1}$) at 461 K; (IV) (B) had $k = 5.4 \times 10^{-4}\ \text{s}^{-1}$ at 392 K; (V) (A) had $k = 5.4 \times 10^{-4}\ \text{s}^{-1}$ at 542.9 K; (VI) (A) had $k = 9.2 \times 10^{-3}\ \text{s}^{-1}$ at 542.9 K.

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