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ON THE TRANSITION STATE FOR DECARBOXYLATION OF β-KETO ACIDS AND βγ-UNSATURATED ACIDS

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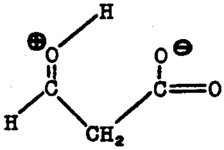
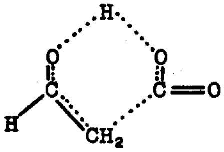
Two descriptions have been used for the decarboxylation of β-keto acids: the first (I) is a dipolar structure (1,2,3) while the second (II) implies synchroneity of all the bond makings and breakings (4). Unfortunately, formulation I has been used rather loosely; it has not been designated specifically as either a transition state or an intermediate. If it is a transition state, bond changes further along the reaction coordinate should have no effect on the reaction rate. This is inconsistent with the observed carboxyl ^{14}C isotope effect (5). If I is an intermediate preceding the transition state, then at first sight there should be no deuterium isotope



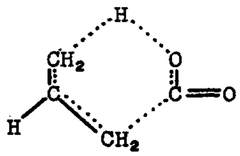
I



II

effect in the reaction. However, if the pre-equilibrium is fast compared with the decarboxylation step, it is possible for the isotope effect in the equilibrium to be shown in the rate determining step (6). Accordingly, the observed deuterium and ^{14}C kinetic isotope effects cannot clearly distinguish between the synchronous formulation II and the unimolecular decomposition of the dipolar intermediate I.

In previous Papers it has been shown that the decarboxylation of βγ-unsaturated acids is a synchronous process, III (7), which exhibits both deuterium and carboxyl ^{14}C kinetic isotope effects (8). The Table compares our own data for the decarboxylation of some 2,2-dimethyl-3-phenylbut-3-enoic acids with Swain's data for the structurally similar benzoylacetic acids (9). The deuterium isotope effects are similar for both series, and the substituent effects are closely comparable. While rates measured at a single temperature should be treated with some reserve, the Table suggests a close similarity of transition state for the two reactions. The data for βγ-unsaturated acids are sparse at present, but those comparisons available point in the same direction. For example α-dimethyl



III

TABLE

Relative Rates and Deuterium Isotope Effects in Decarboxylation

Substituent	Benzoylacetic Acids		2,2-Dimethyl-3-phenyl-but-3-enoic Acids	
	Relative Rate	K_H/K_D	Relative Rate	K_H/K_D
m-NO_2	0.29	2.85	0.30	3.00
p-Cl	0.40	1.67	0.67	1.95
H	1.00	1.40	1.00	2.13
p-CH_3	1.52	0.85	1.97	2.04
p-OCH_3	2.25	1.20	7.75	1.84

acetoacetic acid decarboxylates at 4.5 times the rate of acetoacetic acid (1); α-dimethylbut-3-enoic acid decarboxylates 5.6 times as fast as its parent acid (10).

We have been able to determine the nature of the deuterium kinetic isotope effect in βγ-unsaturated acids. No deuterium exchange was observable in acids recovered from the partial decarboxylation of the deutero βγ-unsaturated acids (as shown by the N.M.R. spectrum). This is in agreement with transition state III and rules out a pre-equilibrium in a formulation similar to I. The above comparisons strongly suggest that II is the better representation for the transition state in the decarboxylation of β-keto acids.

Hammett plots for both series of acids support the conclusion that there is no great polarity in the transition state for either type. The discussion, together with a critical examination of the earlier arguments concerning the transition state in the decarboxylation of β-keto acids will be given elsewhere.

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