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THE ISOMERISATION AND DECARBOXYLATION OF CYCLOPROPANE-1,1-DICARBOXYLIC ACIDS*

by

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A recent publication of Abell and Tien (1) prompts us to publish our results of an investigation on the decarboxylation of cyclopropane-1,1-dicarboxylic acids. These authors have studied the kinetics of the evolution of carbon dioxide from cycloalkane-1,1-dicarboxylic acids. Cyclopropane-1,1-dicarboxylic acid (Ia) is compared with the four-, five- and six-membered ring acids in order to determine the effect of ring size on the rate of decarboxylation. There are some indications (2-4) that cyclopropane-1,1-dicarboxylic acids may not decarboxylate directly like most gem-dicarboxylic acids, but that the primary process is an isomerisation to γ-lactone-carboxylic acids, which decarboxylate

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[*] Part of the forthcoming thesis of J. Bus.

subsequently. Our experiments show that the main product, a γ-lactone is chiefly formed along this route and not by isomerisation of an intermediary cyclopropane-monocarboxylic acid.

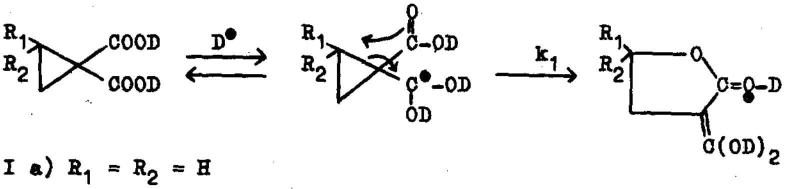
Decarboxylation of Ia (5) in water, in aqueous sulfuric acid and in dilute sodium hydroxide (in sealed tubes) results in the quantitative formation of γ-butyrolactone (IIIa).

2-Methylcyclopropane-1,1-dicarboxylic acid (Ib) (3) gives quantitatively γ-valerolactone (IIIb).

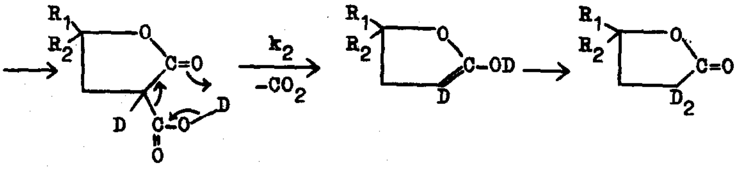
Furthermore we have unequivocally detected (NMR) and isolated (in some cases (4)) the intermediate lactone carboxylic acid (II).

Under the reaction conditions cyclopropane-monocarboxylic acid does not isomerise to γ-butyrolactone.

The following reaction sequence is in full agreement with these results.



I a) $R_1 = R_2 = H$
  b) $R_1 = CH_3$; $R_2 = H$
  c) $R_1 = R_2 = CH_3$



II

III

It appears that the ratio of isomerisation and decarboxylation rates $^{v_1}/_{v_2}$ strongly depends on the acidity of the reaction medium. This ratio is small in water and immeasurably large in concentrated sulfuric acid.

Measurements of the CO_2-evolution of Ia and of IIa (6) under the latter conditions give equal values of the pseudo first order rate constant $k_2 = (13.4 \pm 0.2).10^{-4}sec^{-1}$ * at 394.6°K strongly suggesting that the decarboxylation step is rate determining.

When the reactions are carried out in D_2O, D_2SO_4 and in NaOD (½ equivalent with respect to the deuterated substrate) it turns out by NMR analysis that II as well as III are exclusively deuterated in the α-position. Therefore the formation of olefinic acids with subsequent ring closure to lactones (7) can be ruled out.

We have also observed that log k_1 of the isomerisation of Ia in aqueous D_2SO_4 (2.2 to 8.1 M) is proportional to the Hammett acidity function $-D_0$ (8) (Fig. 1). NaOD considerably slows down the isomerisation.

The activation parameters for the isomerisation of Ia and Ib to IIa and IIb in water have been determined in the usual manner from the data in table I.

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* The average of two kinetic runs with both acids.

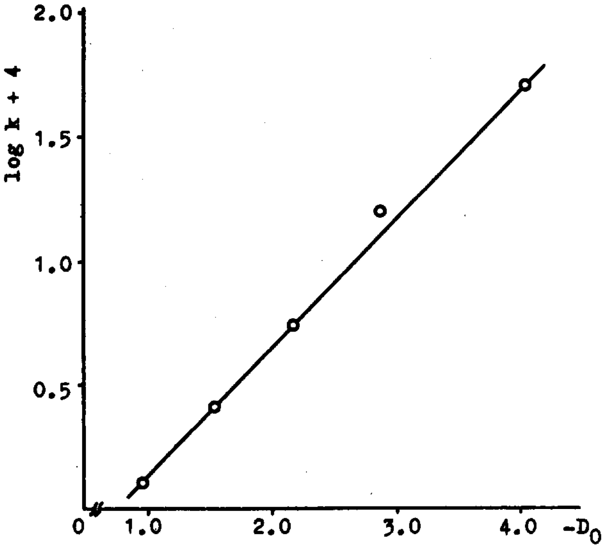

FIG. 1. The Effect of D_0 on the Rates of Isomerisation of Ia in D_2SO_4 at 404.1°K.

TABLE 1

Pseudo First Order Rate Constants for the Isomerisation of Ia and Ib in D_2O.

Ia		Ib	
T°K.	$10^5k_1 sec^{-1}$	T°K.	$10^5k_1 sec^{-1}$
403.3	3.77	363.2	1.94
404.9	4.26	373.2	4.69
412.5	7.40	384.7	10.4
412.9	7.80	393.4	19.8
422.4	15.3	403.1	35.1
422.4	14.5		
433.4	28.8		

For Ia: $\Delta H^* = 23.5$ Kcal/mole; $\Delta S^* = -21$ e.u.

For Ib: $\Delta H^* = 21.0$ Kcal/mole; $\Delta S^* = -23$ e.u.

The dicarboxylic acid Ic has been prepared from isopropylidene malonitrile and diazomethane and subsequent hydrolysis with KOH. In water Ic rapidly isomerises to IIc with a half-life $t_{\frac{1}{2}} \approx 3$ hours at room temperature.

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