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Abstract

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DISSOCIATION CONSTANTS OF SOME SUBSTITUTED CYCLOPROPANE- AND CYCLOPROPENECARBOXYLIC ACIDS

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This article gives the apparent dissociation constants of several substituted cyclopropane- and cyclopropenecarboxylic acids recently obtained in our laboratory ([1–4]), and sets forth certain considerations concerning the influence exerted by the three-membered ring and by the radicals attached to it on the degree of ionization of these acids. Roberts and Chambers ([5]) showed that cyclopropanecarboxylic acid is stronger than other cycloalkanecarboxylic acids, and explained this fact by the increased electronegativity of the carbon atoms forming the three-membered ring ([6,7]). Subsequently, other authors confirmed this result ([8,9]), and also came to the conclusion that the magnitude of the dissociation constant of a substituted cyclopropanecarboxylic acid should be affected by the spatial effects of groups attached to other carbon atoms of the ring.

Table 1

	R_1	R_2	R_3	R_4	pK_A
I	H	C_6H_5 trans *	H	C_6H_5 trans *	5.77
II	H	C_6H_5 trans *	H	C_6H_5 cis *	7.02
III	H	n-C_3H_7 trans *	H	n-C_3H_7 trans *	6.43
IV	H	n-C_3H_7 trans *	H	n-C_3H_7 cis *	6.82
V	H	n-C_4H_9 cis *	H	n-C_4H_9 cis *	7.16
VI	H	C_6H_5 trans *	H	CH_3 trans *	6.06
VII	H	p-$CH_3C_6H_4$ trans *	H	Cl trans *	6.01
VIII	Cl	H	Cl	Cl	3.39
IX	CH_3	H	Cl	Cl	4.62

	R_1	R_2	R_3	R_4	pK_A
X	H	H	COOH	CH_3	5.67
XI	H	H	$C \equiv C—CH_3$	CH_3	5.82

* With respect to the COOH group.

Hammond and Hogle found that the accumulation of bulky groups near the carboxyl group leads to a decrease in the acid strength ([10]), since solvation of its anion by solvent molecules is thereby hindered. According to Odian ([11]), trans-2-phenylcyclopropanecarboxylic acid is stronger than the corresponding cis acid. Shmeikal, Yonash, and Farkash ([12]) measured the pK_A values of a series of stereoisomeric pairs of mono-, di-, and trisubstituted cyclopropanecarboxylic acids and concluded that the degree of ionization of the acids depends to a greater extent on their spatial configuration than on the polar nature of the ring substituents. In this connection, cyclopropanecarboxylic acids having a substituent in the trans position with respect to the carboxyl group proved to be stronger than those having it in the cis position.

In agreement with the rule cited above are also the pK_A values measured by us for cyclopropanecarboxylic * acids (see Table 1).

*

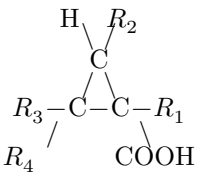

Table 2 gives the values of ΔpK, representing the difference between the pK_a values of two stereoisomeric cyclopropanecarboxylic* acids, which differ from one another in the mutual spatial position of one of the ring substituents and the carboxyl group (cis- or trans-). From the data in Table 2 it is seen that, if the substituent on the ring contains unshared electron pairs or π-electrons of a multiple bond, then ΔpK for the stereoisomeric pair of acids becomes larger than in the case where the substituent is an alkyl group. It seems possible to us to explain this fact by assuming that in the cis acid, which has a substituent with unshared electron pairs or a multiple bond, there is a special interaction of the p- or π-electrons of the substituent with the COOH group (cf. ([13])), leading to a decrease in the strength of the cis acid, i.e., to an increase in ΔpK. Attachment of electron-acceptor groups (Cl, COOH, $C \equiv C—CH_3$) to the cyclopropane ring greatly increases K_A. In strength the acids are arranged in the series (Table 1): VIII > IX > X > XI, i.e., in accordance with the sign and magnitude of the inductive effect of the ring substituents.

Table 2

$$\Delta pK = pK_a - pK_b$$

R	ΔpK	Source
CH_3	0.33	([12])
iso-C_4H_9	0.34	([12])
n-C_3H_7	0.37	see acids III and IV
$(CH_3)_2C{=}CH$	0.54	([12])
C_6H_5	0.68	([12])
iso-C_3H_7O	0.75	([12])

Note. a) R/COOH –trans, b) R/COOH –cis.

Recently Klos and Klos ([14]) synthesized 1,1,2-trimethyl-$\Delta_{2,3}$-cyclopropenecarboxylic-3-acid. This acid proved to be 4.5 times stronger than cis-crotonic acid and three times stronger than benzoic acid, which should be attributed to the increased electronegativity of the carbon atom of the three-membered ring participating in the formation of the double bond ([7,15]).

We measured the pK_A values of 1,2-disubstituted $\Delta_{1,2}$-cyclopropenecarboxylic-3-acids (see Table 3). Since the carboxyl group in these acids is located at a carbon atom that does not participate in formation of the double bond, even the strongest of the acids we measured, XII, proved to be 6.5 times weaker than benzoic acid.

Table 3

	R_1	R_2	pK_A
XII	C_6H_5	CH_3	6.40
XIII	n-$CH_3C_6H_4$	CH_3	6.41
XIV	C_6H_5	C_6H_5	6.49
XV	n-C_4H_9	n-C_4H_9	6.89

The cyclopropane ring transmits polar effects just as weakly as the $-CH_2-CH_2-$ chain ([16–18]). Comparing pK_A for acids XII and XIII, we obtain for the system

$$n\text{-X}-C_6H_4-\underset{\displaystyle \underset{\displaystyle CH_3}{|}}{\overset{\displaystyle C}{|}}-CH-COOH$$

$$\rho < 0.2,$$

i.e., no greater than for the system

$$n\text{-}XC_6H_4{-}CH{-}CH{-}COOH$$

$$CH_2$$

$$(\rho = 0.182).$$

This indicates that introduction of a double bond into positions 1, 2 of the three-membered ring does not lead to an increase in the ability to transmit polar

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$$H_3C \quad CH_3$$

$$\begin{array}{ccc} & C & \\ & / \quad \backslash & \\ H{-}C & & C{-}H \\ & \backslash \quad / \quad \backslash & \\ R & & COOH \end{array}$$

influence of the aryl group on the carboxyl through the ring. Consequently, it may be expected that in the case of cyclopropenecarboxylic acids, steric effects of the substituents should play an important role in ionization. Taking into account the spatial structure of the system, it should be expected that the difficulties in solvation of the anion of 1,2-disubstituted cyclopropenecarboxylic-3-acids will be less than in cis,cis- or cis,trans-1,2-disubstituted cyclopropanecarboxylic-3-acids, but greater than in the corresponding trans-trans acids. Therefore, trans-trans-cyclopropanecarboxylic acids are stronger than cyclopropenecarboxylic acids, while cis,trans- and cis,cis-cyclopropanecarboxylic acids are weaker than cyclopropenecarboxylic acids.

Experimental Part

The dissociation constants of the acids were determined from the half-neutralization point in aqueous-alcoholic (1 : 1 by volume C_2H_5OH) acid solutions by potentiometric titration with a glass electrode at 20° in circuits

with liquid junctions. The concentrations used were $4 \cdot 10^{-3}$ M. No activity corrections were introduced, i.e., apparent ionization constants were determined.

The error of measurement of pK_A was ± 0.015.

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Note: Figure translations are in progress. See original paper for figures.