Inductive Constants for the Cyclohexenyl, Cyclohexenylmethyl, Cyclopentenyl, and Cyclopentenylmethyl Groups

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In connection with a study of neighbouring double bond participation in cyclopentenylalkyl and cyclohexenylalkyl systems, Taft's σ* constants were determined for cyclopent-1-, -2-, and -3-enyl, cyclopent-1-, -2-, and -3-enylmethyl, cyclohex-1-enyl, and cyclohex-1-, -2-, and -3-enylmethyl groups as well as for the corresponding saturated substituents which have not been reported before. It was shown that the presence of the double bond significantly affects the polar characteristics of the group and that this effect depends on its position in the ring. The negative values for cyclohex-1-enyl and cyclopent-1-enyl groups do not agree with the electron-withdrawing effect of αβ-unsaturated substituents in open chain systems.

DOUBLE-BOND participation in the solvolysis of cycloalkenyl systems have been the subject of numerous investigations. All were based on reaction product analysis and/or kinetic measurements.[1] Youssef and Sharaf [1a] summarized these investigations concluding that double-bond participation in cycloalkenyl systems is observed when the double bond in the cyclic system is separated from the carbon carrying the leaving group by an odd number of carbon atoms.

TABLE 1

Second-order rate constants for acid and base hydrolysis at 25.0° in 70% (v/v) acetone–water

Compound	k/l mol^{-1} s^{-1} Base hydrolysis	Acid hydrolysis
Ethyl acetate [a]	5.71×10^{-2}	4.80×10^{-5}
Ethyl cyclohexylmethanecarboxylate	$(2.25 \pm 0.1) \times 10^{-3}$	$(3.50 \pm 0.1) \times 10^{-6}$
Ethyl cyclohex-1-enylmethanecarboxylate	$(1.10 \pm 0.1) \times 10^{-2}$	$(5.80 \pm 0.1) \times 10^{-6}$
Ethyl cyclohex-2-enylmethanecarboxylate	$(4.70 \pm 0.1) \times 10^{-3}$	$(3.20 \pm 0.1) \times 10^{-6}$
Ethyl cyclohex-3-enylmethanecarboxylate	$(3.36 \pm 0.1) \times 10^{-3}$	$(4.04 \pm 0.1) \times 10^{-6}$
Ethyl cyclopentylmethanecarboxylate	$(3.34 \pm 0.07) \times 10^{-3}$	$(5.17 \pm 0.2) \times 10^{-6}$
Ethyl cyclopent-1-enylmethanecarboxylate	$(1.73 \pm 0.01) \times 10^{-2}$	$(6.47 \pm 0.3) \times 10^{-6}$
Ethyl cyclopent-2-enylmethanecarboxylate	$(5.80 \pm 0.1) \times 10^{-3}$	$(3.50 \pm 0.3) \times 10^{-6}$
Ethyl cyclopent-3-enylmethanecarboxylate [d]	$(5.14 \pm 0.01) \times 10^{-3}$	$(5.03 \pm 0.2) \times 10^{-6}$
Ethyl cyclohexanecarboxylate [b]	$(1.85 \pm 0.1) \times 10^{-3}$	$(7.05 \pm 0.2) \times 10^{-6}$
Ethyl cyclohex-1-enecarboxylate	$(0.91 \pm 0.1) \times 10^{-3}$	$(2.46 \pm 0.2) \times 10^{-6}$
Ethyl cyclohex-3-enecarboxylate [c]	$(5.12 \pm 0.05) \times 10^{-3}$	$(8.88 \pm 0.2) \times 10^{-6}$
Ethyl cyclopentanecarboxylate	$(3.54 \pm 0.1) \times 10^{-3}$	$(1.41 \pm 0.1) \times 10^{-5}$
Ethyl cyclopent-1-enecarboxylate	$(1.74 \pm 0.1) \times 10^{-3}$	$(6.60 \pm 0.4) \times 10^{-6}$
Ethyl cyclopent-2-enecarboxylate	$(1.79 \pm 0.09) \times 10^{-2}$	$(7.13 \pm 0.2) \times 10^{-6}$
Ethyl cyclopent-3-enecarboxylate	$(1.91 \pm 0.01) \times 10^{-2}$	$(2.21 \pm 0.1) \times 10^{-5}$

[a] Ref. 2b. k_B 5.4×10^{-2}, k_A 4.6×10^{-5} l mol^{-1} s^{-1}. [b] Ref. 2b. k_B $(1.74 \pm 0.03) \times 10^{-3}$, k_A $(7.2 \pm 0.4) \times 10^{-6}$ l mol^{-1} s^{-1}. [c] Ref. 2b. k_B $(4.86 \pm 0.00) \times 10^{-3}$, k_A $(8.88 \pm 0.4) \times 10^{-6}$ l mol^{-1} s^{-1}. [d] From two measurements.

To gain more general information concerning the mechanism of these reactions for five- and six-ring atom systems, we planned to apply Schleyer's [2] approach which correlates the rate constants for the compounds being investigated with the constants of related model alkyl systems using Taft σ* constants.[2b] For this purpose it was necessary to determine the σ* constants for these substituents. In this paper we report the results which are based on the fundamental definition of σ* in terms of rates of acidic and basic ethyl ester hydrolysis. Some of the σ* values have already been reported [1b] and they are included in Table 1 together with the results of our experiments. The rate constants for acid and base hydrolysis (Table 1) were determined as average values from at least three measurements.

The data from Table 1 were inserted into Taft's equation [3] and the σ* values in Table 2 were obtained. The deviations ascribed to these values are based on the observed deviations in the rate constants of Table 1. The values given in Table 2 for cycloalkylmethyl and cycloalkenylmethyl groups are in agreement with the classical theory of the polar effect. Certainly doubts which are present when small σ* values are used as a measure of polar effects of substituents have to be kept in mind when dealing with the results presented in this paper.

TABLE 2

Polar substituent constants for cyclohexenylmethyl and cyclopentenylmethyl substituents

Substituent	log $(k/k_0)_B$	log $(k/k_0)_A$	σ*
Cyclohexylmethyl	-1.40	-1.14	-0.10 ± 0.01 [a]
Cyclohex-1-enylmethyl	-0.71	-0.92	$+0.08 \pm 0.01$
Cyclohex-2-enylmethyl	-1.08	-1.18	$+0.03 \pm 0.01$
Cyclohex-3-enylmethyl	-1.23	-1.07	-0.06 ± 0.01
Cyclopentylmethyl	-1.23	-0.97	-0.11 ± 0.01
Cyclopent-1-enylmethyl	-0.52	-0.87	$+0.14 \pm 0.01$
Cyclopent-2-enylmethyl	-0.99	-1.14	$+0.06 \pm 0.01$
Cyclopent-3-enylmethyl	-1.04	-0.98	-0.03 ± 0.01

[a] Ref. 4. σ* -0.06.

The σ* values for cyclohexenylmethyl and cyclopentenylmethyl groups show that the difference in the number of ring atoms has no effect on the electron-releasing ability of these groups. This is in accord with experiments in open-chain systems which have shown that the effect of lengthening the carbon chain beyond three carbon atoms[5] is negligible. The presence of the unsaturated function in the ring significantly changes the polar characteristics of the substituent in such a way that it introduces an electron-withdrawing effect which diminishes with the separation between the double bond and the functional group. This effect is opposite to the electron-releasing one of the rest of the molecule. Isomeric groups in the 1- and 2-positions have a small but definite electron-withdrawing effect which conforms well with the electronegative characteristics of sp^2 carbon atoms. A comparison of the σ^* values for cyclohexenylmethyl and cyclopentenylmethyl groups shows that the effect of the double bond in three comparable pairs is more pronounced in the cyclopentyl system.

The attempt to correlate the σ^* values (Table 3) for the cyclohexenyl and cyclopentenyl groups with the distance between the functional group and electronegative sp^2 carbon atoms failed. The negative σ^* values for cyclohex-1-enyl and cyclopent-1-enyl, indicating the electron-releasing effect of these groups, do not agree with the effect of the same groups in the corresponding carbinyl systems as well as with the effect of αβ-unsaturated in open-chain systems,[6] which is known to be electron withdrawing. This suggests either the operation of a novel factor in these two molecules or an unusual interaction of known factors. The slower rates of both alkaline and acidic hydrolysis of these compounds compared with the corresponding rates of acetates could be explained by resonance. The fact that alkaline hydrolysis is affected much more than acidic, which leads to the negative σ^* value and which is not the case in open-chain systems, needs further investigation. The σ^* value for cyclohex-2-enyl could not be determined experimentally, but by considering the value of σ^* for the corresponding carbinyl group and using the magnitude of the damping effect of the methylene group in the corresponding cyclopentenyl system ($\sigma^*_{\text{cyclopent-2-enyl}}/\sigma^*_{\text{cyclopent-2-enylmethyl}} = 2.17$) it could be calculated to be +0.06.

TABLE 3

Polar substituent constants for cyclohexenyl and cyclopentenyl substituents

Substituent	$\log (k/k_0)_B$	$\log(k/k_0)_A$	σ^*
Cyclohexyl[a,b]	−1.48	−0.83	−0.26 ± 0.01
Cyclohex-1-enyl	−1.80	−1.29	−0.20 ± 0.01
Cyclohex-3-enyl[c]	−1.05	−0.73	−0.13 ± 0.01
Cyclopentyl[d]	−1.21	−0.53	−0.27 ± 0.02
Cyclopent-1-enyl	−1.52	−0.86	−0.26 ± 0.02
Cyclopent-2-enyl	−0.50	−0.83	+0.13 ± 0.01
Cyclopent-3-enyl	−0.48	−0.34	−0.06 ± 0.01

[a] Ref. 1*b*. σ^* −0.26 ± 0.02. [b] Ref. 4. σ^* −0.15. [c] Ref. 1*b*. σ^* −0.12 ± 0.02. [d] Ref. 4. σ^* −0.20.

Cyclopent-3-enyl and cyclohex-3-enyl groups have electron-releasing effects which, compared with the effects of saturated analogues, are decreased by the presence of two electronegative sp^2 carbon atoms.

The values $\log (k/k_0)_A$ (Table 3, third column) which by definition are steric substituent constants (E_S)[7] for the cyclohexyl and cyclopentyl groups, agree well with the previously reported values[8] showing an increase in value with ring size. The increase is evident in all other corresponding pairs. The E_s values for cyclohex-1-enyl and cyclopent-1-enyl cannot be considered a measure of the steric effects since the effect of resonance between the substituents and the ester group in the initial state also contributes.

EXPERIMENTAL

Preparative details of the compounds used are given in Supplementary Publications No. SUP 22372 (6 pp.)*

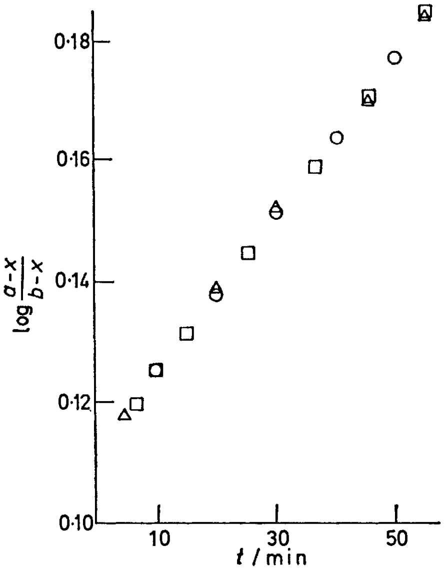

FIGURE 1 Plot of $\log[(a - x)/(b - x)]$ against time for the alkaline hydrolysis of ethyl cyclohex-3-enecarboxylate. a = initial concentration of hydrolysing agent; b = initial concentration of ester. ○, $k_{\text{exp. 1}}$ 5.107×10^{-3}; □, $k_{\text{exp. 2}}$ 5.116×10^{-3}; △, $k_{\text{exp. 3}}$ 5.131×10^{-3} l mol^{-1} s^{-1}

Kinetic Measurements.—(a) *Alkaline hydrolysis*. Except in the case of ethyl acetate, 0.1M-ester solutions were prepared at room temperature by dissolving the necessary amount of ester in anhydrous acetone (70 ml) and diluting with water (30 ml). In the case of ethyl acetate 0.4M aqueous solution was prepared and this solution (30 ml) diluted with acetone (70 ml). The concentration of each ester solution was checked before use by complete hydrolysis and back titration with acid.

The infinite titres for three separately prepared solutions with the same amount of ester for each case agreed to less than 1%.

For the alkaline hydrolysing agent, 0.33M-sodium hydroxide (30 ml) was diluted with acetone (70 ml). The concentration of this solution was determined by titration immediately before use.

After the ester and base solutions had both equilibrated at 25.0°, 50 ml of each solution was transferred into a 100 ml volumetric flask which was stoppered, well shaken, and quickly returned to the thermostat. The reaction was followed by withdrawing portions (5 ml) at suitable intervals, running them into 0.05N-hydrochloric acid (10 ml)

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin I*, 1977, Index issue.

and finally titrating the excess acid with 0.05N-sodium hydroxide solution against phenolphthalein.

An example of the experiments is presented in Figure 1.

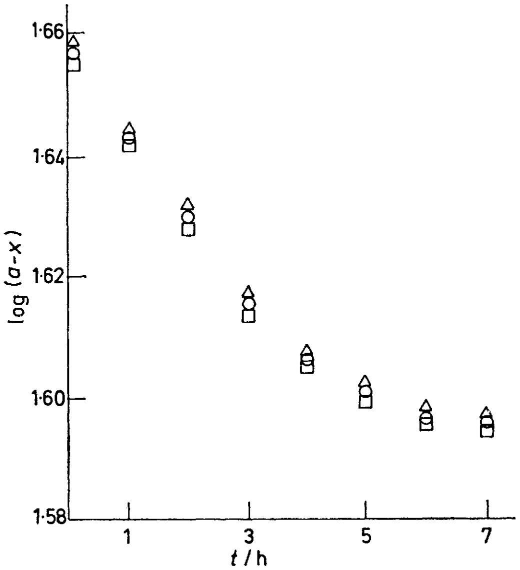

FIGURE 2 Plot of log$(a - x)$ against time for the acid hydrolysis of ethyl cyclohex-3-enecarboxylate. a = initial concentration of ester. △, $k_{\text{exp. }1}$ 8.83×10^{-6}; ○, $k_{\text{exp. }2}$ 8.89×10^{-6}; □, $k_{\text{exp. }3}$ 8.92×10^{-6} l mol^{-1} s^{-1}

In most cases the hydrolysis proceeded to *ca.* 70% completion and the rate constants were calculated from the expression: $k = 2.303/t(a - b)[\log b(a - x)/a(b - x)]$.

(b) *Acid hydrolysis.* The ester and hydrochloric acid solutions were prepared as described above. Because of the slow rate of reaction and the volatility of the solvent, portions (5 ml) were sealed in glass ampoules and equilibrated at 25.0°. At suitable intervals the contents of a tube were titrated with sodium hydroxide solution.

The values of k, calculated from the expression $k = 2.303/t[\log a/(a - x)]$, fell with time. To evaluate k, we plotted $\log(a - x)$ against time, and k was obtained from the slope of the tangent at zero time.

An example of the experiments is presented in Figure 2.

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