Charge Development and Mechanism in Disrotatory Ring Opening of Cyclopropyl Bromides

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The temperature dependence of the rates of hydrolysis of *cis*- and *trans*-2-vinylcyclopropyl bromides has been determined in water. The temperature coefficient of the enthalpy of activation ($\Delta C_p{}^{\neq}$) for both compounds was unusual (-27 and -35 cal mol^{-1} deg^{-1}). From this fact, it was concluded that the charge development at the transition state was low, in agreement with the conclusions of Clark and Smale (19). The slightly inverse α-deuterium isotope effect ($k_H/k_D = 0.994$) is consistent with that conclusion.

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On a déterminé la variation, en fonction de la température, des vitesses d'hydrolyse dans l'eau des isomères *cis* et *trans* du bromure de vinyl-2 cyclopropyle. La valeur du coefficient de température de l'enthalpie d'activation ($\Delta C_p{}^{\neq}$) pour les deux composés est exceptionnelle (-27 et -35 cal mol^{-1} deg^{-1}). On en conclut qu'à l'état de transition la charge est peu developpée. Ceci est en accord avec les conclusions de Clark et Smale (19). L'effet isotopique légèrement inverse du deutérium-α ($k_H/k_D = 0.994$) est consistant avec cette conclusion.

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Introduction

In this paper we present evidence bearing on the degree of charge development at the transition state for the hydrolysis of *cis*- and *trans*-2-vinylcyclopropyl bromides and from these observations draw conclusions concerning mechanism.

Solvolytic studies of cyclopropyl derivatives have attracted attention for many years (1–8). Initially there was the question of apparent inertness of such compounds to solvolysis, *e.g.* 170 °C was required to give a specific rate constant of 4.7×10^{-5} s^{-1} (9). Brown attributed this inertness to the unfavorable angle strain, "I-strain" (10, 11). Alternatively, the less than normal internal bond angle (60°) was judged to contribute to excess s-character (12, 13) and hence to stabilize exocyclic bonds of the cyclopropane ring (14). In contrast to these arguments advanced to account for unusual inertness, in 1961, Schleyer and Nicholas (15), noting the even more pronounced stability of 7-norbornyl tosylate toward acetolysis, argued that the cyclopropyl tosylate actually reacted faster than might be predicted from a consideration of the internal bond angles. The authors suggested a kind of anchimeric assistance to provide an extra driving force equivalent to a factor of 10^2 in the rate (15).[3] Further insight into the mechanism of ring opening of cyclopropyl derivatives came with the development of the Woodward–Hoffmann rule governing concerted reactions (16). According to that rule, ring opening of the cyclopropyl cation to allyl cation is allowed in the disrotatory mode.[4] Independently, De Puy and co-workers (18) arrived at the conclusion that the ring opening is governed by the stereochemistry of the leaving group.

Recently Schleyer and co-workers (1, 2) in their extensive studies of the solvolysis of cyclopropyl derivatives in acetic acid proposed that the degree of ring opening at the transition state of the cyclopropyl halides and sulfonates was considerable, "a protoallylic transition state". As a consequence, charge delocalization to the β-positions was extensive. However, Clark and Smale (19) from a consideration of their theoretical calculations and the ρ^+ values obtained by

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[3] Schleyer's recent estimate is at least a factor of 10^5; see ref. 2.

[4] Except for deamination reactions (17), allyl derivatives were the only product found for unsubstituted or β-substituted monocyclic systems.

De Puy and co-workers (20), suggested that the transition state for the acetolysis of cyclopropyl derivatives was reached at an early stage in the ring-opening and that the angle of rotation could not be over 45°.

While recognizing that studies of solvolysis in water may not resolve the above difference of interpretation, nevertheless it would be useful to investigate charge development at the transition state for the solvolysis of such compounds in water. If the conclusion of Clark and Smale is valid, then the results obtained for hydrolysis in water would have bearing on the interpretation of evidence relative to charge development in other solvents.

The inability of cyclopropyl systems to stabilize positive charge has been fairly well established.[5] As charge increases in the activation process during solvolysis, it is accepted (1, 2, 18, 20, 23) that a concerted back-side overlap of the C_2—C_3 bond on the developing p-orbital of the C_1 carbon (*i.e.* ring opening) provides the necessary stabilization. Therefore charge development and ring opening are co-related. However a different view was suggested by Schleyer and co-workers (1).[6]

A large body of empirical data now exists which provides a basis for estimating the relative degree of charge development at the transition state for ionogenic reactions in water from the temperature coefficient of the enthalpy of activation. This estimation is based on the unique structural properties of water, the nature of solvation of weakly polar solutes in water and the effect of charge development accompanying the activation process (24, 25). In the activation process for ionogenic reactions the requirement for solvent reorganization is a temperature dependent component of $\Delta H^{\ddagger}$ which varies with the extent to which water structure is reorganized or more correctly, disorganized. This disorganization is dependent not only on the degree of charge development but also on the nature of the displaced group, the degree of reorganization for leaving groups having the same charge level being: arenesulfonate = methanesulfonate ≪ bromide, chloride, iodide < nitrate.[7] The enthalpy requirement for reorientation of the solvating water molecules decreases as the temperature increases[8] and the extent of this effect is reflected in the rate measurements provided the latter are made with sufficient accuracy. Clearly, this is but one source of a temperature dependency of $\Delta H^{\ddagger}$ (26–29) and care must be exercised to exclude other contributions such as impurities or the possibility of mixed kinetics before drawing conclusions from $(\delta\Delta H^{\ddagger}/\Delta T)_p$ with respect to the extent of solvent reorganization. Where there is reason to believe that the reaction is uncomplicated, values of $(d\Delta H^{\ddagger}/dT)_p = \Delta C_p^{\ddagger}$ for displacement of halides from primary carbon are found to lie in the range -40 to -50 cal deg^{-1} mol^{-1}; from secondary carbons -60 cal deg^{-1} mol^{-1} and from tertiary carbons -80 to -100 cal deg^{-1} mol^{-1} (19). There are exceptions. Thus 4-methylbenzyl chloride gives a value of -79 cal deg.$^{-1}$ mol^{-1}, and cyclopropylcarbinyl chloride (a primary chloride) and cyclobutyl chloride (a secondary halide) which are presumed to undergo rearrangement to nonclassical ions in the activation process give values of $\Delta C_p^{\ddagger}$ of -81 and -107 cal deg^{-1} mol^{-1}, respectively (30). In the absence of water-structure-breaking functional groups near the reaction site (31, 32) compounds showing pronounced anchimeric assistance and hydrogen participation (33) likewise give more negative $\Delta C_p^{\ddagger}$ values than would be expected in the absence of such assistance. This observation is consistent with an approach to a limiting mechanism. Thus normal values of $\Delta C_p^{\ddagger}$ may be taken as evidence that the mechanism of hydrolysis is similar to the class to which the reactant belongs. Values outside of the normal range may be taken as evidence of some alternative mechanistic explanation provided spurious contribution to $\Delta C_p^{\ddagger}$ have been eliminated. Thus the temperature dependence of $\Delta H^{\ddagger}$ for the particular case of hydrolysis in water provides a useful mechanistic probe, even

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[5] See ref. 9, 21; however, see ref. 22.

[6] Reference 1, p. 140.

[7] This applies for the nitrate group where the mechanism tends to S_N1.

[8] It is obvious that this is but one of the posssible interpretations since a negative temperature coefficient for $\Delta H^{\ddagger}$ would be found if the solvation of the developing ion increased with an increase in temperature or if the degree of charge development at the transition state increased with temperature or both. These possibilities cannot be excluded on the available evidence. Reasons for believing that the breakdown of the initial state structure is the dominant factor in determining the observed negative temperature coefficient of $\Delta H^{\ddagger}$ have been outlined previously (24).

though the $\Delta H^{\ddagger}$ values alone have proven of little analytical value.

From the beginning of this investigation it was recognized that the conclusions based on the values of $\Delta C_p^{\ddagger}$ obtained for hydrolysis in water need not necessarily apply to transition state characteristics in other solvent. However, as will be shown in the discussion, the particular systems under investigation here may be exceptional in this regard.

Results and Discussion

The rate data were determined conductometrically and are generally good to better than 0.5% for repetitive runs (the *trans* compound gave better reproducibility). The standard error within a particular determination of the specific rate constant was usually better than 0.1%. The discrepancy between cells has been attributed to variations in absorption of the reactants and possibly differential adsorption of ions at the walls, an inherent difficulty at the low concentrations imposed by meagre solubility of the reactants. The use of larger cells would reduce this difficulty but introduces other complications. The methods used were consistent with past practise (24). The rate constants as a function of temperature are fitted to the empirical formula

$$[1] \qquad \log k = A_1 + A_2/T + A_3 \log T$$

assuming $\mathrm{d}\Delta C^{\ddagger}/dT = 0$, an assumption which is imposed by experimental errors and probably is not too serious over the relatively short temperature range available (60–94 °C). The corresponding empirical constants are given in Table 1. The average specific rate constants over a range of temperatures can then be calculated from eq. 1 and Table 1. The method of Clarke and Glew (25, 27, 34) for the treatment of the temperature dependence of equilibrium data was modified to accommodate kinetic rate data and to compute the pseudothermodynamic parameters (Table 2).

TABLE 1. Empirical constants for the three-parameter equation (eq. 1) for the hydrolysis of *cis*- and *trans*-2-vinylcyclopropyl bromides

2-Vinylcyclopropyl bromide	A_1	$-A_2$	$-A_3$	n*
trans	62.3978	8393.1382	16.4042	34_{59}^{91}
cis	51.5332	8194.3581	12.7857	51_{70}^{95}

*$n_{T_2}{}^{T_1}$ = number of rate determination; T_1 and T_2 give the temperature range over which the rates were determined.

The negative values of the $\Delta C_p^{\ddagger}$ derived from the temperature dependence of the rate of hydrolysis (-35 ± 2 and -27 ± 4 cal deg^{-1} mol^{-1}) are surprisingly low:[9] lower, in fact, than had been found previously for the hydrolysis of any other alkyl halide (24). Careful purification excluded the possibility that the results were spurious as a consequence of impurities.[10] In consequence we were led to the inevitable conclusion that either the transition state was reached at a lower degree of charge development than had been found previously for the hydrolysis of even primary halides, or the results were, in both cases, a consequence of "mixed kinetics" or "partitioning" (26, 27, 29, 35).

A comparison of the values of $\Delta C_p^{\ddagger}$ obtained in this study with those from the hydrolysis of other allylic halides is useful (Table 3). Allyl chloride and β-methylallyl chloride have values of -50 cal deg^{-1} mol^{-1}. α-Methylallyl chloride, which might be expected to have a transition state resembling that of a S_N1 reaction has a value of -92 cal deg^{-1} mol^{-1}. The latter is consistent with a large degree of charge development at the transition state and provides an obvious contrast to the values of $\Delta C_p^{\ddagger}$ obtained in this study.

Having excluded impurities as a possible explanation for these less negative values of $\Delta C_p^{\ddagger}$, we consider three possibilities: (*i*) partitioning, (*ii*) mixed kinetics, and (*iii*) that the low values of $-\Delta C_p^{\ddagger}$ simply reflect a lower degree of charge development at the transition states than has been observed previously for the displacement of a halide.

The fact that the α-deuterium isotope effect (Table 4) is negligible argues against any important structural change. However, it is doubtful even if the cyclopropyl group opened up to give a fully conjugated allylic cation at the transition state, that a large isotope effect would be observed (36, 37). At best it is consistent with the proposed concerted "internal" S_N2 type reaction. A much stronger argument against the formation of an intimate ion-pair such as implied

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[9] Low and high refer to the absolute values of $\Delta C_p^{\ddagger}$.

[10] Impurities, however, need not always lead to a low negative value of the $\Delta C_p^{\ddagger}$; see ref. 27.

TABLE 2. Pseudothermodynamic quantities for the hydrolysis of *cis*- and *trans*-2-vinylcyclopropyl bromides in water

2-Vinylcyclopropyl bromide	T (°C)	$\Delta H^{\ddagger}$ (cal mol^{-1})	$\Delta S^{\ddagger}$ (cal deg^{-1} mol^{-1})	$-\Delta C_p^{\ddagger}$ (cal deg^{-1} mol^{-1})
trans	75	26 363±10	1.29±0.03	35±2
cis	75	27 957±28	0.85±0.08	27±4

TABLE 3. Derived thermodynamic parameters for the hydrolysis of allyl chlorides in water*

Compound (chloride)	T (°C)	$\Delta H^{\ddagger}$ (cal mol^{-1})	$\Delta S^{\ddagger}$ (cal deg^{-1} mol^{-1})	$\Delta C_p^{\ddagger}$ (cal deg^{-1} mol^{-1})
Allyl	40	22 495±25	−10.12±0.08	−50
β-Methylallyl	40	21 469±121	−11.69±0.37	−49
α-Methylallyl	40	21 585±85	0.04±0.3	−92
trans-γ-Methylallyl	30	22 712±44	3.36±0.14	−82
cis-γ-Methylallyl	40	21 331±21	−3.68±0.07	−66

*Reference 22.

TABLE 4. Rate constants, α-deuterium isotope effects, and the *m* values for the hydrolysis of *cis*- and *trans*-2-vinylcyclopropyl bromides

2-Vinylcyclopropyl bromide	T (°C)	k ($\times 10^{-4}$ s^{-1})	m (aqueous alcohol)	k_H/k_D	Reference
cis	95	0.246 (50% EtOH)			4
	95	2.928 (H_2O)	0.59	0.993	This work
trans	95	2.65 (50% EtOH)			4
	95	32.067 (H_2O)	0.59	0.995	This work

by the possibility of partitioning is to be found in the shape of the energy diagram for the opening of the cyclopropyl ring plotted against the angle of rotation as calculated by Clark and Armstrong (38) and by Radom *et al.* (39). These authors show that ring opening in the cyclopropyl system is characterized by a steady steep decrease in energy, hence the existence of a solvent (water) stabilized charge intermediate seems as unlikely as it is unnecessary.

As an alternative mechanism, the unusually low values of $-\Delta C_p^{\ddagger}$ found for these compounds can be attributed to "mixed kinetics", *i.e.* two reactions with different $\Delta H^{\ddagger}$ values occurring in competition. In such a situation the reaction with the higher $\Delta H^{\ddagger}$ value becomes more important as the temperature rises and this results in a positive contribution to $\Delta C_p^{\ddagger}$ combining to reduce the magnitude of the combined normal negative values (28). Such a rationalization is as difficult to prove as to disprove in the present system and the following citations are offered for consideration only. Parham and Yong (40) in attempting to account for the product found in the solvolysis of *cis*- and *trans*-1,1-dichloro-2,3-dipropylcyclopropane, suggested that the ring opening process is accompanied by solvent attack concerted with ionization. Since there are two nonequivalent sites for nucleophilic interaction in our system the above mechanism could provide for the lower negative values of $\Delta C_p^{\ddagger}$. This rationalization would imply two transition states each one occurring at a degree of charge development normal for an S_N2 displacement but with sufficiently different $\Delta H^{\ddagger}$ values to account for the more positive than normal $-\Delta C_p^{\ddagger}$ values. That both *cis* and *trans* isomers should have approximately the same compensating effect is possible but seems unlikely. Product analysis offers no assistance here.

An abnormally low value for $\Delta C_p^{\ddagger}$ for a reaction which might be expected to react by an S_N1-like mechanism is not without precedent. Ko and Robertson have shown recently (41) that the values of $\Delta C_p^{\ddagger}$ for the hydrolysis of a series of sulfamoyl chlorides shift from −76 cal deg^{-1} mol^{-1} for dimethylsulfamoyl chloride to −39 cal deg^{-1} mol^{-1} for the diethyl homolog. In the latter, other evidence shows that hydrogen participation occurs and crowding about the sulfur is enhanced. The rate is increased eight-fold over the dimethyl homolog. While charge dispersal may account for some decrease in $\Delta C_p^{\ddagger}$, this could hardly be a sufficient explanation and the possibility that the transition state coincides with the formation of the shared hydrogen bond must be regarded as a distinct possibility.

Thus in the absence of evidence to the contrary, it seems probable that for the hydrolysis of the 2-vinylcyclopropyl bromides, of the several possibilities the simpler hypothesis is sufficient, *i.e.* that the unusually low negative values of $\Delta C_p^{\ddagger}$ obtained in this study give evidence of the transition state having a relatively small charge development on the displaced group and consequently the transition state comes relatively early in the ring opening process. Such a conclusion would be consistent with the conclusion of Clark and Smale (19), the ρ^+ values obtained by DePuy and co-workers (20)[11] for analogous systems (though in a different solvent, acetic acid) and would tend to minimize the differences in $\Delta C_p^{\ddagger}$ between different leaving groups (40). Research on related systems aiming to confirm the generality of this conclusion is now in progress. Even if evidence were uncovered supporting mixed kinetics rather than the simpler hypothesis cited above, the low values of $\Delta C_p^{\ddagger}$ obtained here would still probably imply that the transition state for the ring opening of cyclopropyl halides and hence charge development was at a very early stage, much less advanced than for the corresponding hydrolysis of methyl halides (24).

Experimental

Tri-*n*-butyltin hydride was made in the usual way (43, 44). The physical properties and the n.m.r. spectrum agreed with the literature (45–47).

Tri-*n*-butyltin deuteride was made according to the procedure of Martin and Landgrebe (48, 49) in 60% yield: b.p. 50° (0.02 mm) lit. (48) 78° and up (0.6 mm); the n.m.r. (CCl_4) spectrum showed no signal at τ 5.21.

1,1-Dibromo-2-vinylcyclopropane was prepared by the addition of dibromocarbene to 1,3-butadiene (4, 50–52): b.p. 36–37° (5 mm) (lit. (50, 51) 76–82° (50 mm), (4) 53–56° (10 mm), and (51) 70° (26 mm)); n.m.r. (CCl_4) gave complex multiplet at τ 7.8 and 8.4 (3H, ring protons) and 4.6 (m, 3H, vinyl protons); the mass spectrum gave parent peaks at *m/e* 224, 226, 228 (1:2:1), significant fragments at 66 ($C_5H_6^+$), 65, 39 and 145, 149 (1:1) ($C_5H_6Br^+$), however no complete analysis was possible because the compound was not pure[12] and not so stable[13].

cis- and *trans*-2-Vinylcyclopropyl bromides were made by the reduction of 1,1-dibromo-2-vinylcyclopropane with tri-*n*-butyltin hydride (53) in 60% yield: b.p. 58–62° (80 mm) (lit. (4, 51) 60–74° (90 mm)). The isomers could not be separated by spinning band distillation but were isolated in pure form by passing through the preparative g.c. using a 20 ft × 3/8 in. QF-1 column (90°). The *trans* isomer was eluted first (4): the mass spectrum gave parent peaks at *m/e* 146, 148 (1:1), base peak at 67 ($C_5H_7^+$), and significant fragments at 41 and 39; n.m.r. (CCl_4) gave complex multiplets at τ 4.2–5.16 (3H, vinyl protons), 7.14–7.42 (1H, C*H*Br), 7.9–8.35 (1H, ring proton), and 8.6–9.1 (2H, ring protons). The *cis* isomer gave exactly the same mass spectrum as the *trans* compound, however the n.m.r. (CCl_4) gave complex absorption at τ 4.1–5.05 (3H, vinyl protons), 6.7–7.6 (1H, C*H*Br), 8.1–8.85 (2H, ring protons), and 9.06–9.23 (1H, ring proton). Both isomers were checked again by g.c. using a 20% FFAP on Carbowax W column.

cis- and *trans*-2-Vinylcyclopropyl-1-*d* bromides were made by the reduction of 1,1-dibromo-2-vinylcyclopropane with tri-*n*-butyltin deuteride (53) in 40% yield: b.p. 52–60° (78–74 mm). The pure isomers were obtained as described above. The mass spectrum of the *trans* isomer gave parent peaks at *m/e* 147, 149 (1:1), and significant fragments at 68 ($C_5H_6D^+$, base peak), 42, 41, 40, and 39; n.m.r. (CCl_4) gave complex absorption at τ 4.2–5.15 (3H, vinyl protons), 7.95–8.33 (q, 1H, ring proton), 8.63–8.90 (m, 2H, ring protons). The *cis* isomer again showed exactly the same mass spectrum as the *trans* compound; n.m.r. (CCl_4) gave τ 4.10–5.20 (complex, 3H, vinyl protons), 8.16–8.73 (m, 2H, ring protons), 9.03–9.22 (t, 1H, ring proton). Both isomers showed no C*H*Br signal and the α-deuterium content should be at least 97%.

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[11] The ρ^+ values were found to be -1.75 for the β-substituted and -4.31 for the α-substituted cyclopropyl tosylates (43). Whatever the magnitude these indicate a relatively lower degree of charge development at the β-carbons compared to that at the α-carbon. Therefore at least for the phenyl substituted cyclopropyl derivatives it seems that the cyclopropyl ring does not open up beyond 45° of rotation (19).

[12] The impurities $CHBr_3$, CH_2Br_2 are present. Low intensity but distinct peaks are observable at 196, 198, 200 (1:2:1) corresponding to the loss of C_2H_4, at 184, 186, 188 (1:2:1) corresponding to the loss of C_3H_4 and at 158, 160, 162 (1:2:1) (Br_2^+). However a weak dibromo triplet at 211, 213, 215 (1:2:1) cannot be accounted for.

[13] The freshly distilled dibromo compound is colorless but turns yellow on standing at room temperature.

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