

Electrostatic Participation by Carboxylate Groups in Forming α -Lactones

F. G. BORDWELL AND A. C. KNIPE

Department of Chemistry, Northwestern University, Evanston, Illinois 60201

Received September 4, 1969

Rates of hydrolysis for α -bromophenylacetic acid and six of its *meta*- and *para*-substituted derivatives have been measured in aqueous sodium bicarbonate at two or more temperatures. The substantial negative value for the Hammett ρ (-2.94) and the large positive activation enthalpies and entropies indicate a zwitterion-like transition state for the ionization of Br^- from ArCHBrCO_2^- . Rate-structure correlations show that the order of (electrostatic) participation by the α - CO_2^- group is tertiary bromide > secondary bromide > primary bromide, which is just opposite to that observed for covalent participation. It is suggested that the α - CO_2^- group exerts an electron-withdrawing inductive effect. This is counteracted in the hydrolysis reaction by electrostatic participation, which provides "ionizing power" sufficient to level the effects of adding water or salts to the medium for this carbonium ion reaction.

The observation that the solvolysis of α -bromopropionate ion in dilute basic media is independent of base concentration and occurs with retention of configuration¹ is generally regarded as classical example of neighboring group participation.²⁻⁸ It was originally suggested that this was an $\text{S}_{\text{N}}1$ reaction, and that configuration was retained in a zwitterion intermediate.¹ Most subsequent investigators have, however, favored an α -lactone intermediate to account for the stereochemistry.²⁻⁸ Even if an α -lactone is accepted an intermediate the question as to whether the transition state for halide ion release is lactone-like or zwitterion-like remains unanswered. This question is difficult to answer.³ If the α - CO_2^- group initiates an intramolecular nucleophilic displacement the transition state will be lactone-like, but the stereochemistry can also be explained if ionization of the C-Br bond is merely facilitated by the presence of the negative charge on the carboxylate group and ionization is followed by a rapid collapse to an α -lactone. The rate of bromide ion release for the hydrolysis of $\text{CH}_3\text{CHBrCO}_2^-$ is actually retarded by ninefold, relative to $\text{CH}_3\text{CHBrCH}_3$. The latter is much more sensitive to the ionizing power of the solvent, however, so that when the comparison is made in methanol $\text{CH}_3\text{CHBrCO}_2^-$ is about 20-fold faster.⁸ Although these data have been interpreted as "good evidence that the rate-determining step of the solvolysis involves direct intramolecular displacement by the carboxylate group,"⁸ this conclusion is difficult to accept until the electrostatic effect of the α - CO_2^- group has been assessed. The small rate increases observed on increasing the polarity of the medium through increased water content or on addition of salts is in the direction predicted for a zwitterion-like transition state, but is smaller than might have been anticipated. At first sight one might have expected a reaction involving a lactone-like transition state to be retarded by an increased polarity or the medium, but Grunwald and Winstein got around this difficulty by assuming that the

α -lactone itself "has very high ionic character," and that a lactone-like transition state would be expected to have increased ionic character, relative to the ground state.³ Their conclusion was that the transition state is lactone-like, and most authors have accepted this interpretation.⁶⁻⁸ On the other hand, Gould has interpreted the small positive salt effect as evidence that C-Br bond breaking is the slow step, and that the α -lactone is formed in a rapid subsequent step.⁵ In order to obtain additional information concerning the nature of the transition state in the solvolysis of α -halo carboxylates we have examined substituent effects on the hydrolysis rates in the ArCHBrCO_2^- system.⁹ These results are reported in the present paper and are compared in the following paper with a similar study of the $\text{ArCHBrCH}_2\text{CO}_2^-$ and ArCHBrCHBrCO_2^- systems.

Results

The rate of hydrolysis of α -bromophenylacetic acid and six of its *meta*- and *para*-substituted derivatives in aqueous sodium bicarbonate were measured at two or more temperatures. The reactions were followed by potentiometric determination of bromide ion released, at intervals. Reactions of each compound was found to be of first order in bromoacetate ion and of zero order in base. Plots of $\log [\text{ArCHBrCO}_2^-]$ vs. t were found to be linear to at least three half-lives; rate constants were evaluated from the slope of the least squares "best fit" by multiplying by 2.302. The results are summarized in Table I.

The product of the reaction was in each instance the corresponding mandelic acid (>95%).

The values at 25° differ somewhat from those reported by Kemp and Metzger.⁹ Their values, obtained by titration of liberated acid in 0.681 *M* acetone at ionic strength of 0.551 using excess sodium hydroxide, were consistently higher than those obtained by us (*H*, +6.5%; *p*-Cl, +9.6%; *m*-NO₂, +36%; *p*-NO₂, +35%). For the parent and *p*-Cl compounds correction for salt effect⁹ brings the two sets of data closely in line. For the *m*-NO₂ and *p*-NO₂ compounds there is a hydroxide contribution to the rate.⁹ When this and the salt effect are taken into consideration, the agreement is reasonably good.

For the parent compound and its *p*-Cl derivative our enthalpies of activation (determined from the rates at four temperatures) are 1.2 and 1.4 kcal/mol higher

(1) W. A. Cowdry, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 1208 (1937); 1243 (1938).

(2) S. Winstein and H. J. Lucas, *J. Amer. Chem. Soc.*, **61**, 1576 (1939); S. Winstein, *ibid.*, **61**, 1635 (1939).

(3) E. Grunwald and S. Winstein, *ibid.*, **70**, 841 (1948).

(4) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," 2nd ed, Cornell University Press, Ithaca, N. Y., 1969, p 524.

(5) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., Inc., New York, N. Y., 1959, p 270.

(6) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962, p 116.

(7) J. Hine, "Physical Organic Chemistry," McGraw-Hill, New York, N. Y., 1962, p 142.

(8) B. Capon, *Quart. Rev. (London)*, **18**, 75 (1964).

(9) After this investigation was essentially complete a similar study was reported by K. C. Kemp and D. Metzger, *J. Org. Chem.*, **33**, 4165 (1968).

TABLE I

KINETIC DATA FOR THE HYDROLYSIS OF α -BROMOPHENYLACETIC ACIDS (0.006 M) IN AQUEOUS SODIUM BICARBONATE (0.066 M)

Bromoacetic acid	Registry no.	T, °C ^a	10 ³ k, b, c sec ⁻¹	ΔH^\ddagger , kcal/ mol ^d	ΔS^\ddagger , eu
<i>p</i> -Methylphenyl	25297-16-9	0.0	351		
		25.0	19,700	25.5	19
		40.7	5720		
<i>m</i> -Methylphenyl	25297-17-0	0.0	5.84		
		25.0	601	28.4	22
		40.7	5720		
Phenyl	4870-65-9	0.0	2.8		
		25.0	293	27.8	18
		40.7	3000		
		50.0	8700		
<i>p</i> -Chlorophenyl	3381-73-5	0.0	1.58		
		25.0	150	27.9	17
		40.8	1650		
		50.0	4980		
<i>m</i> -Chlorophenyl	3381-74-6	25.0	15.9	29.8	20
		40.8	238		
		50.0	797		
<i>m</i> -Nitrophenyl	21986-02-7	25.0	3.06	28.3	11
		50.0	121		
		61.0	620		
<i>p</i> -Nitrophenyl	4578-72-7	25.0	1.65	29.3	13
		50.0	81.7		
		61.0	367		

^a The values for runs at 25° are the mean of three combinations of concentrations of ArCHBrCO₂⁻ and NaHCO₃, e.g., 0.006 M vs. 0.066 M or 0.036 M and 0.003 M vs. 0.036 M. The standard deviations did not exceed $\pm 3\%$ for any of the runs. ^b All reactions were followed to three half-lives or beyond. ^c Correlation coefficients (r) were in every instance 0.997 or better. ^d Correlation coefficients (r) for the Arrhenius plot were in every instance 0.9994 or better.

than those reported and our entropies of activation are 3–4 eu higher. For *m*-NO₂ there is close agreement in the enthalpies from the two investigations, but our ΔS^\ddagger value is ca. 4 eu lower in this instance.

A Hammett plot of the data obtained at 25° using σ^+ values for *p*-Cl and *p*-Me substituents gave $\rho = -3.42$ (correlation coefficient = 0.979). A considerably larger $\sigma^+_{p\text{-Me}}$ value (ca. -0.55 rather than -0.311) would be required to fit the line.¹⁰ Excluding the *p*-Me substituent $\rho = -2.94$ at 25° ($r = 0.995$). This compares with a value of -2.66 obtained by Kemp and Metzger.⁹

The ρ values determined at 40.8 and 50.0° from plots excluding the *p*-Me substituent were -2.83 ($r = 0.999$) and -2.64 ($r = 0.999$), respectively.

The effect of solvent on the rate was determined for PhCHBrCO₂⁻ at 25° using aqueous ethanol. The slope (m) is 0.17 for a Grunwald–Winstein plot of $\log k$ vs. Y (for five points, $r = 0.999$; $\log k_0 = -4.24$). A small solvent effect has been reported for CH₃CHBrCO₂⁻,⁸ and for ArCHBrCO₂⁻.⁹

Discussion

Substituent Effects.—The substantial negative ρ value (-2.94) and the better fit of the data with σ^+ constants rather than σ constants for *p*-Me and *p*-Cl substituents provide strong evidence for the development of appreciable ionic character in the C–Br bond during hydrolysis of ArCHBrCO₂⁻. As has been

pointed out by Kemp and Metzger, the incipient benzylic cation in this reaction is more sensitive to substituent effects than are the incipient cations derived in the solvolyses of benzyl chlorides in aqueous alcohol or aqueous acetone ($\rho = -2.2$ and -1.8), or benzyl tosylates in aqueous ethanol ($\rho = -2.2$), but are much less sensitive than the incipient benzyl cations derived from the formolyses of benzyl bromides or benzyl tosylates ($\rho = -5.5$ and -6.0).⁹ The effects are comparable with those observed in the hydration of styrenes ($\rho = -3.4^{11a}$), the hydration of α -methylstyrenes ($\rho = -3.2^{11b}$), and the dehydration of 2-aryl-2-propanols ($\rho = 3.1^{11b}$) which are pictured as having the “positive charge partially on the incoming (or outgoing) proton and partially delocalized into the arene system.”^{11b} For ArCHBrCO₂⁻ the developing positive charge is partially neutralized by the negative charge on the carboxylate group. Therefore, the data seem to require a zwitterion-like transition state where participation is electrostatic in nature, rather than an α -lactone-like transition state where participation involves covalent bond formation.

It would be desirable to have information concerning the size and sign of ρ for other systems reacting by electrostatic or covalent bonding participation. The only systems studied to date which can be used as models are participation by carbanions in the Ramberg–Bäcklund reaction¹² (for ArCHBrSO₂CH₃, $\rho = +1.27$; for ArCHBrSO₂CH₂Ph, $\rho = +1.55$; for ArCHClSO₂CH₂Ph, $\rho = +1.64$) and participation by alkoxide ion in the formation of styrene oxides (for the reaction ArCHBrCH₂OH + HO⁻, $\rho = -1.13$).¹³ The positive ρ values for the Ramberg–Bäcklund reaction suggest that covalent participation by a carbanion is aided by electron-withdrawing groups. On the other hand, the sizable negative ρ for styrene oxide formation suggests that with the more weakly nucleophilic oxide ion the carbon atom being attacked may develop appreciable positive character. It is not certain whether the latter is an example of covalent or electrostatic participation. More data are needed, therefore, to give a clear-cut interpretation to the meaning of the sizable negative ρ for ArCHBrCO₂⁻ hydrolysis, but we favor electrostatic participation since it appears to give the more consistent overall picture of the hydrolyses in the ArCHBrCO₂⁻, ArCHBrCH₂CO₂⁻, and ArCHBrCHBrCO₂⁻ systems, as will be brought out below and in the succeeding paper.

Activation Parameters.—The activation parameters for the ArCHBrCO₂⁻ hydrolyses are noteworthy for the high activation enthalpies, and particularly for the large positive activation entropies (Table I). The latter are considerably more positive than the 0 to 10 eu range that is characteristic for most unimolecular (A-1, SN1) solvolyses,¹⁴ and far greater than the 0 to -30 eu range into which bimolecular (A-2, SN2) sol-

(11) (a) W. M. Schubert, B. Lamur, and J. R. Keefe, *ibid.*, **86**, 4727 (1964); (b) N. C. Deno, F. A. Kish, and H. J. Peterson, *ibid.*, **87**, 2157 (1965).

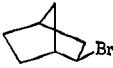
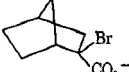
(12) M. D. Wolfinger, Ph.D. Dissertation, Northwestern University, June 1968. These are overall ρ values measured in 40% aqueous dioxane. If corrected for the influence of the substituent on the sulfone \rightleftharpoons sulfone carbanion equilibrium the values should be decreased by about 0.5 unit.

(13) A. C. Knipe, unpublished results. This value would be decreased to ca. -1.01 if corrected for the influence of substituents on the ArCHBrCH₂OH + HO⁻ \rightleftharpoons ArCHBrCH₂O⁻ + H₂O equilibrium.

(14) L. L. Schaleger and F. A. Long, *Advan. Phys. Org. Chem.*, **1**, 1 (1963).

(10) The apparent $\sigma^+_{p\text{-Me}}$ value for the hydrolysis of benzyl tosylates and chlorides is -0.63 ; see J. K. Kochi and G. S. Hammond, *J. Amer. Chem. Soc.*, **75**, 3445 (1953).

TABLE II
 KINETIC DATA FOR THE HYDROLYSIS OF α -HALO CARBOXYLATES AND RELATED ALKYL HALIDES

Halide	T , °C	k , sec ⁻¹	$k_{CO_2^-}/k_H$	ΔH^\ddagger	ΔS^\ddagger	Ref
CH ₃ Br	50	1.05×10^{-5}				a
CH ₂ BrCO ₂ ⁻	50	$(1.1 \times 10^{-6})^b$	0.1	24.6	-9.5	c
CH ₃ CH ₂ Br	55	1.8×10^{-5}				a
CH ₃ CHBrCO ₂ ⁻	55	$(4.2 \times 10^{-5})^b$	2.3	29.7	11.4	d
	25	4.17×10^{-7}				
(CH ₃) ₂ CHBr	25	$(3.7 \times 10^{-6})^b$				e
(CH ₃) ₂ CBrCO ₂ ⁻	25	1.21×10^{-4}	33	25.8	3.3	23
PhCH ₂ Br	50	$(\sim 2.5 \times 10^{-3})^f$				
PhCHBrCO ₂ ⁻	50	8.7×10^{-3}	3.5	27.8	18	Table I
PhCHBrCH ₃	25	5.6×10^{-1}		19.2	5	g, h
	50	$(6.9)^g$				
	62	$(6.55 \times 10^{-1})^h$		21	-17	18
	62	$(7.25 \times 10^{-4})^h$	1.1	28	11	18

^a S. Winstein, E. Grunwald, and H. W. Jones, *J. Amer. Chem. Soc.*, **73**, 2700 (1951). ^b Extrapolated. ^c C. A. Kingsbury, *ibid.*, **87**, 5409 (1965). ^d H. Heine, E. Becker, and J. F. Lane, *ibid.*, **75**, 4514 (1953). ^e K. T. Lefk, R. E. Robertson, and S. E. Sugamori, *Can. J. Chem.*, **39**, 1990 (1961). ^f Estimated from data obtained for PhCH₂Cl. ^g A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, **79**, 1602 (1957). ^h In 80% EtOH.

volyses usually fall.¹⁴ Strongly positive ΔH^\ddagger and ΔS^\ddagger values have been observed previously for the hydrolysis of α -bromoisobutyrate ions. The latter has been the subject of an unusually careful, quantitative study, which included a determination of the heat capacity of activation and the solvent deuterium isotope effect.¹⁵ The conclusion of Robertson is that the hydrolysis of α -bromoisobutyrate ion almost certainly occurs by an S_N1 mechanism.¹⁵ The activation parameters for hydrolysis of Me₂CBrCO₂⁻ (ΔH^\ddagger , 28.96 kcal/mol; ΔS^\ddagger , 20.6 eu) are remarkably similar to those of the ArCHBrCO₂⁻ system (Table I). The evidence from activation parameters would appear, then, to strongly favor electrostatic participation rather than covalent participation by the carboxylate group of ArCHBrCO₂⁻. According to this view the carboxylate grouping provides "ionizing power," perhaps by controlling intramolecular reorganization of solvent molecules, which makes this S_N1 reaction immune to the large rate acceleration ordinarily observed on increasing the water or salt content of the medium.¹⁶

Correlation of Rate and Structure.—Participation of a neighboring group ordinarily leads to appreciable rate acceleration. For example, neighboring β O⁻, SR, NH₂, and I groups cause rate accelerations over that of parent chloride (k/k_H) of 10³- to 10⁸-fold.¹⁷ By comparison, the effect of the neighboring carboxylate group is very modest. Comparison of the rates of hydrolysis of various α -bromoalkanecarboxylates with the rates of hydrolysis of the parent alkyl bromides are summarized in Table II.

Examination of Table II shows that substitution of the carboxylate group for a hydrogen of methyl bromide causes a tenfold retardation in the hydrolysis

(15) B. N. Hendy, W. A. Redmond, and R. E. Robertson, *Can. J. Chem.*, **45**, 2071 (1967).

(16) See ref 15 for a detailed discussion of the possible role of the CO₂⁻ group in affecting solvation during the reaction. The remarkable insensitivity of the solvolyses of α -bromoalkanecarboxylate ions to solvent ionizing power may be judged by comparing the following k_{H_2O}/k_{MeOH} ratios: CH₃CHBrCO₂⁻, 2.4 (at 50°); (CH₃)₂CBrCO₂⁻, 2.4 (at 64°); PhCHBrCO₂⁻, 6 (at 25°); *i*-PrBr, 270 (at 50°); *t*-BuBr, 1700 (at 25°). (The latter data are taken from ref 6, except for that for PhCHBrCO₂⁻, which was calculated using $m = 0.17$.)

(17) S. Winstein and E. Grunwald, *J. Amer. Chem. Soc.*, **70**, 828 (1948).

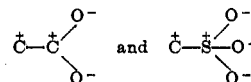
rate. On the other hand, substitution into ethyl, isopropyl, benzyl, or *exo*-norbornyl bromides causes a moderate rate acceleration (between *ca.* 2- and 33-fold). The effect in the series BrCH₂CO₂⁻, CH₂CHBrCO₂⁻, (CH₃)₂CBrCO₂⁻ is atypical in that it is greatest for the tertiary bromide and least for the primary bromide. This is just the reverse of usual participation effects,¹⁷ and provides an additional argument for electrostatic rather than covalent participation. The greater participation in tertiary than in primary systems will be even more marked in solvents of lower ionizing power than in water. It is of interest to note that extensive rearrangement occurs during the solvolysis of *exo*- α -bromonorbornanecarboxylate ion,¹⁸ which is suggestive of carbonium ion intermediate.

Comparison shows that for PhCH₂Br substitution of a methyl group causes *ca.* a 2700-fold increase in hydrolysis rate, whereas substitution of a carboxylate group cause only *ca.* 3.5-fold increase. It seems most likely that for the latter electrostatic participation is being offset by an electron-withdrawing effect of the CO₂⁻ group.¹⁹⁻²²

Another piece of qualitative evidence favoring electrostatic participation in the hydrolysis of PhCHBrCO₂⁻ (S_N1 mechanism) is the close similarity in the leaving group effects for the PhCHXCO₂⁻ and Ph-

(18) W. R. Vaughan, R. Caple, J. Csapilla, and P. Scheiner, *ibid.*, **87**, 2204 (1965).

(19) In *meta* and *para* positions on the benzene ring the CO₂⁻ group appears to have a weak electron-releasing effect, as judged from its effect on the ionization constants of benzoic acids and the solvolysis rates of cumyl chlorides.²⁰ On the other hand, in the ionization of ArPO₃H⁻,²¹ the saponification of ArCO₂Et,²¹ or the saponification of ArOCOCH₃,²¹ the CO₂⁻ appears to be electron withdrawing. Coulomb's law applied to



indicates a net repulsion by both the CO₂⁻ and SO₃⁻ groups to the development of an adjacent positive charge. The SO₃⁻ group is sufficiently electron-withdrawing to make ⁻O₃SCH₂CO₂H a stronger acid by 0.7 pK_a units than CH₃CO₂H.²²

(20) Y. Okamoto and H. C. Brown, *ibid.*, **80**, 4976 (1958).

(21) See the summary by V. van Bekkum, P. E. Verkade, and B. M. Wepter, *Recl. Trav. Chim. Pays-Bas*, **78**, 815 (1959).

(22) R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, p 99.

CHXCH₃ systems ($k_{Br}/k_{Cl} \cong 12/1$ in each instance at 25° in water).^{23,24} In contrast, the leaving group effects for covalent participation to form three-membered rings appears to be unusually large.²⁵

Hydrolysis of optically active PhCHBrCO₂⁻ or Ph-CHClCO₂⁻ leads to essentially racemic mandelic acid.²⁹ This result can be rationalized either by assuming the formation of a zwitterion intermediate of lifetime long enough to permit racemization or of an α -lactone intermediate which racemizes, presumably *via* the zwitterion, prior to capture by solvent.

In the following paper it will be shown that participation by the carboxylate ion is more effective in accelerating the overall rate for β -CO₂⁻ than for α -CO₂⁻. Since for covalent participation formation of a three-membered ring is always much more effective than formation of a four-membered ring, this is further support for the electrostatic participation hypothesis. (This takes no account, of course, of internal return, which would be much greater for the α -CO₂⁻ system.)

Experimental Section

Aryl α -Bromoacetic Acids.—These compounds were prepared by methods described in the literature.^{10,30}

- (23) A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, **79**, 1602 (1957).
 (24) W. R. Buleraig and H. M. Dawson, *J. Chem. Soc.*, 80 (1943).
 (25) For the Ramberg-Bäcklund reaction of α -halo sulfones k_{Br}/k_{Cl} varies from 88 to 620 depending on the system, solvent, and temperature.²⁵ For ethylene oxide formation from HOCH₂CH₂X initiated by base $k_{Br}/k_{Cl} \cong 88/1$ in water, and ca. 153/1 in aqueous methanol, after correcting for the alcohol ionization constants.^{27,28} For ArCHXCH₂OH $k_{Br}/k_{Cl} = 55$ in water.²⁹
 (26) F. G. Bordwell and J. M. Williams, Jr., *J. Amer. Chem. Soc.*, **90**, 435 (1968).
 (27) C. L. McCabe and J. C. Warner, *ibid.*, **70**, 4031 (1948).
 (28) A. C. Knipe, unpublished results.
 (29) (a) A. McKenzie and G. W. Clough, *J. Chem. Soc.*, **93**, 811 (1908); **95**, 777 (1909). (b) A. McKenzie and N. Walker, *ibid.*, **107**, 1685 (1916); A. M. Ward, *ibid.*, **118**, 1184 (1926).
 (30) J. Krapcho, U. S. Patent 3,166,554 [*Chem. Abstr.*, **62**, 13157e (1965)]; B. Ekstrum, A. Gomes-Revilla, R. Mollberg, H. Thelin, and B. Stoberg, *Acta Chem. Scand.*, **19** (1), 281 (1965); K. Heyns and H. Schultze, *Justus Liebigs Ann. Chem.*, **611**, 55 (1958); B. Wladislaw and A. Giora, *J. Chem. Soc.*, 5747 (1965).

Kinetics of Solvolysis of α -Bromophenylacetic Acid Anions.—Reaction was initiated by adding a weighed amount of the bromo acid to a base solution (0.03–0.07 M NaHCO₃ in water or 0.016 M NaOH in ethanol–water mixtures) that had attained the temperature of the thermostated bath. The mixture was agitated until dissolution was complete. The time taken for dissolution of the acid was disadvantageous in cases where the reaction half-life was short. This was overcome by dissolving the material in acetone (2 drops) prior to addition, whereupon dissolution was immediate. Insensitivity of reaction rate to the small concentration of acetone was verified.

Aliquot parts (containing 0–6 microequivalents of bromide ion) were withdrawn at intervals and quenched in a solution of acetone (3 ml) and 0.25 M nitric acid (5 ml). Bromide ion was titrated potentiometrically with 0.0015 N AgNO₃ using an automatic constant rate buret (Sargent Model C) linked with a chart recorder. The electrode assembly comprised a silver indicator and calomel half-cell reference electrode. The end point was determined from the inflection of a volume vs. mV trace in the usual way. It was confirmed that the presence of unreacted material and of reaction products was without effect on the titrations.

Product Analysis.—The bromo acid (0.005 mol) was kept with aqueous 0.06 M sodium bicarbonate (250 ml) at 50° for ten half-lives. The reaction mixture was acidified (HCl) to pH 5 and evaporated to a 50-ml volume. The solution was saturated with sodium chloride and continuously extracted with ether during a 100-hr period. The extract was dried (MgSO₄) and evaporated. In each case the corresponding mandelic acid was isolated in not less than 96% yield (based on the mass of crude material which in general melted 5° below the literature value). The purified products were identified by ir, nmr, and mixture melting point.

α -Bromo-*m*-methylphenylacetic Acids.—A mixture of *m*-methylmandelic acid (3.32 g, 0.02 mol) and 48% hydrobromic acid (10 ml) was refluxed during 3 hr. The mixture was poured onto crushed ice (30 g) and extraction was with ether. The ether extract was washed with water to remove unreacted mandelic acid, dried, and evaporated to give the product (1.5 g, 33% yield). The bromo acid had bp 134° (0.5 mm).

α -Bromo-*p*-methylphenylacetic Acid.— α -Bromo-*p*-methylphenylacetic acid was prepared from *p*-methylmandelic acid (0.02 mol) in 25% yield, in the same way as the *m*-methyl analog. It had bp 145° (0.1 mm) and mp 83°.

Acknowledgment.—We are grateful to the National Science Foundation (GP 7065) for support of this investigation.

Electrostatic Participation by Carboxylate Groups in the Hydrolysis of β -Bromo- and α,β -Dibromo- β -arylpropionate Ions

F. G. BORDWELL AND A. C. KNIPE

Department of Chemistry, Northwestern University, Evanston, Illinois 60201

Received September 4, 1969

The rates of bromide ion release from β -bromo- β -phenylpropionate ion and five of its *meta*- and *para*-substituted derivatives, ArCHBrCH₂CO₂⁻ (1), have been measured in aqueous sodium bicarbonate solution at three or more temperatures. The sizable negative ρ (-3.24 at 25°) and the insensitivity of the rate to salt and solvent effects has been interpreted as evidence for electrostatic participation in bromide ion release by the β -CO₂⁻ leading to a zwitterion intermediate which partitions itself between styrene and β -lactone products. The positive activation entropies are consistent with this interpretation, as are correlations of rate with structure. Salt, solvent, and substituent effects similar to those of 1 were observed also for the rate of bromide ion release from *erythro*- α,β -dibromo- β -phenylpropionate ion and five of its *meta*- and *para*-substituted derivatives ($\rho = -3.19$ at 37.8°). Here the zwitterion intermediate decomposes mainly to β -bromostyrenes.

Beginning with Einhorn's isolation of a β -lactone from the reaction of β -bromo-*o*-nitrohydrocinnamic acid with sodium carbonate,¹ there have been numerous examples wherein β -halo carboxylates have been shown to undergo hydrolysis to give β -lactones as inter-

mediates or as final products.² The hydrolysis of chlorosuccinate ions was demonstrated by Holmberg to involve β -lactone intermediates,³ and these were

(2) For reviews, see (a) H. E. Zaugg, *Org. React.*, **8**, 315 (1954); (b) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962, pp 116–119; (c) B. Capon, *Quart. Rev., Chem. Soc.*, **18**, 75 (1964).

(3) B. Holmberg, *J. Prakt. Chem.*, **88**, 553 (1913).

(1) A. Einhorn, *Ber.*, **16**, 2208 (1883).