Organic and Biological Chemistry

The Volume of Activation in Unimolecular Decomposition Reactions. Decarboxylation and Demercuration

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Abstract: Volumes of activation have been measured for several nonionogenic demercuration and decarboxylation reactions. The fact that all are positive is harmonious with the supposition that the activation process is dominated by bond breaking. The variation of activation volume with solvent polarity for decarboxylation of carboxylate ions indicates that the negative charge is more localized in the transition state than in the ground state. This evidence also suggests that delocalization increases in the series $CF_3^- < CCl_3^- < CBr_3^-$. The activation volumes for malonic acid point to a dipolar transition state, and the behavior of picolinic acid indicates a depolarization in the transition state.

Previous studies have shown that rate processes involving nonionogenic bond rupture have substantial positive volumes of activation. Examples are the decomposition of aromatic diazonium salts,[1] *t*-alkylsulfonium salts,[2] alkyl and acyl peroxides,[3] 2,2'-azobisisobutyronitrile,[4] and pentaphenylethane.[4] It is also found that reactions in which the rate-controlling step is the nonionogenic decomposition of an intermediate have positive volumes of activation.[5,6] These observations can provide a deep insight into the properties of the transition state since the elongation of the breaking bond can be calculated by dividing the cross-sectional area of the activated complex into the activation volume. Because the reactions produce no new ions, it is reasonable to assume that surrounding solvent molecules do not undergo a change of volume, but it is desirable to obtain supporting evidence by showing that the activation volume is not dependent on solvent polarity. Owing to side reactions and limited solubilities, such evidence is available for only one of the reactions above,[2] but the decomposition reaction of carboxylate ions and the recently discovered demercuration reaction[7] seemed likely to behave well in a variety of solvents.

The mechanisms of decarboxylation reactions and the effect of structure on their rates have considerable intrinsic interest, and a general survey of the subject has recently become available.[8] The mechanistic implications of activation volumes are coming to be fairly well understood,[9] and thus the current hypothetical models for the transition states in decarboxylation reactions can be subjected to a new stringent test. In particular, the decarboxylation of β-keto acids and picolinic acids may involve large changes in electrical polarization during the activation process, and activation volumes are well suited to the detection and estimation of such effects.[2]

Results and Discussion

Demercuration. It has been recently reported[7] that alkylmercuric ions (RHg^+) in association with very weakly nucleophilic anions undergo a first-order decomposition into metallic mercury and carbonium ions. The SN1 mechanism is postulated on the basis of stereochemistry (chiefly racemization with slight inversion) and measurement of a small and nearly constant change in free energy of activation when the solvent is changed from water to acetic acid. The development of carbonium ion character in the transition state is judged to be nearly complete as evidenced by the extreme increase of reactivity in the series $1° < 2° < 3°$.

The volumes of activation for methyl-, ethyl-, and isopropylmercuric ions in water are, respectively: 0, 6, and 9 ml/mole. The reaction of the *t*-butyl compound is too rapid to permit its inclusion in this series. It was necessary to use a range of temperatures from 174.0 (methyl) to 46.4° (isopropyl) in order to obtain reasonable reaction times, and evidence is therefore needed that the activation volume is not strongly temperature dependent. Another determination for methylmercuric ion at 140.0° gave the same value within experimental error (1 ml/mole).

The use of ethanol as a solvent for the decomposition of ethylmercuric ion has been reported in a brief communication,[7] but we have found that the following side reaction interferes seriously, at least at temperatures

$$C_2H_5Hg^+ + C_2H_5OH \longrightarrow C_2H_6 + CH_3CHO + Hg + H^+$$
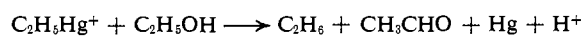
near 100°. The prospect of finding an organic solvent which readily dissolves ionic solutes and would resist oxidation by RHg^+ seemed to dim for further pursuit.

(1) K. R. Brower, *J. Am. Chem. Soc.*, **82**, 4535 (1960).
(2) K. R. Brower, *ibid.*, **85**, 1401 (1963); K. R. Brower and J. Chen, *ibid.*, **87**, 3396 (1965).
(3) C. Walling and G. Metzger, *ibid.*, **81**, 5365 (1959); C. Walling and J. Pellon, *ibid.*, **79**, 4786 (1957).
(4) A. H. Ewald, *Discussions Faraday Soc.*, **22**, 138 (1956).
(5) E. Whalley, *Can. J. Chem.*, **39**, 597, 1094, 1101 (1961).
(6) W. Le Noble and M. Duffy, *J. Am. Chem. Soc.*, **86**, 4512 (1964).
(7) F. R. Jensen and R. J. Ouellete, *ibid.*, **83**, 4477, 4478 (1961); **85**, 363, 367 (1963).
(8) E. M. Kosower, "Molecular Biochemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, Section 2.2.
(9) S. D. Hamann, "High Pressure Physics and Chemistry," Vol. II, R. S. Bradley, Ed., Academic Press Inc., New York, N. Y., 1963, Chapter 8.

Table I

Reactant	Solvent	Temp, °C	ΔV^*, ml/mole
Methylmercuric fluoroborate	Water	174.0	0
		140.0	0
Ethylmercuric fluoroborate	Water	114.0	6
Isopropylmercuric fluoroborate	Water	46.4	9
Malonic acid	Water	115.0	5
	Methyl sulfoxide	81.3	0
	Dioxane	111.2	−7
	Tetrahydrofuran	100.0	−10
Dimethylmalonic acid	Water	125.0	5
Acetoacetic acid	Water	40.0	4
Picolinic acid	Water	180.0	17
	Ethanol	165.0	19
Monosodium malonate	Water	125.0	3
Monosodium dimethyl-malonate	Water	140.0	2
Sodium benzoylacetate	Water	54.4	5
Sodium dimethylacetoacetate	Water	66.4	5
	Methanol	45.0	−3
Sodium phenylpropiolate	Water	102.0	10
	Methanol	102.0	10
Sodium p-nitrophenylacetate	Water	129.0	11
	Methanol	114.4	10
Sodium trifluoroacetate	Water	163.0	8
	Ethanol	163.0	0
Sodium trichloroacetate	Water	80.0	10
	Ethanol	60.5	4
Sodium tribromoacetate	Water	66.0	8
	Ethanol	30.4	6

The variation of activation volume for the three alkyl groups is unexpected. It is improbable that it reflects differences in the degree of bond stretching because Hammond's postulate[10] would require greatest stretching for the least reactive substance, methylmercuric ion. Furthermore, it is implausible that the latter would have a zero activation volume unless some compensating decrease of volume comes from another source. A possibility is nucleophilic assistance by solvent which could contribute as much as −10 ml/mole if the bimolecular character is fully developed,[11] and would be greatest for the least hindered methyl substrate. The evidence for predominance of SN1 character in the reactions of secondary and tertiary alkylmercuric ions is strong, but the energy of the unsolvated methyl cation might be prohibitive in comparison to that of the SN2 activated complex or a hydrid of the two.

The activation volumes for ethyl- and isopropylmercuric ion are comparable to those of t-butyl- and t-amylsulfonium ions[2] which are, respectively, +10 and +14 ml/mole. The smaller magnitudes probably reflect the smaller cross-sectional area of the mercury atom as leaving group. If the effectve radius of the latter is assumed to be 1.44 A, then the bonds to the ethyl and isopropyl groups are elongated by 1.6 and 2.3 A, respectively. Owing to the crudity of the molecular model it would be unwise to emphasize the difference between these values.

Decomposition of Carboxylic Acid Salts. Ready decarboxylation of a salt is associated with the formation of a carbanion which is weakly basic. The weakness of the unshared electron pair may be due to one or more causes such as delocalization into a π orbital,

excessive s character, or strong inductive displacement. We have attempted to encompass all of these effects in our study by measurements on salts of β-keto acids, phenylpropiolic acid, and trihaloacetic acids which are thought to exhibit the effects in the order named. The volumes of activation are recorded in Table I.

Contrary to our *a priori* judgment, several of the carboxylate ions show a variation of activation volume with solvent polarity. In every such case the ethanol or methanol solution gives the smaller volume, and one may conclude that the transition state is more tightly solvated than the carboxylate ion.[2] The component of volume associated with bond stretching would be somewhat larger than the net value for water solutions. Since ions cause approximately twice as much constriction of ethanol or methanol as of water, the correction term would be roughly equal to the difference in activation volume for the two solvents. Thus for dimethylacetoacetate ion, the corrected volume would be 5 + [5 − (−3)] = 13 ml. Where the variation with solvent is absent as in sodium phenylpropiolate (+10 ml) or sodium p-nitrophenylacetate (+10 ml), it can be concluded that bond stretching is the sole factor contributing to the activation volume. For trifluoro- and trichloroacetate ions the corrected values of 16 ml each seem abnormally large in comparison to the values above and those of diazonium ion decomposition[1] (10 ml) and t-alkylsulfonium ion solvolysis[2] (10–14 ml). It is interesting to note that the activation volume for the generation of dichlorocarbene from chloroform is also surprisingly large.[6]

The influence of solvent can be rationalized by assuming that the transition state exhibits almost complete separation of the carbanion and carbon dioxide molecule, and that the variations of activation volume with solvent are due to variations in localization of the charge of the carbanion. Where the charge would be chiefly concentrated on one atom as in the enolate ions derived from β-ketocarboxylates or the trifluoromethide ion derived from trifluoroacetate, the activation volumes show decreases of 8 ml each on changing from water to methanol or ethanol. On the other hand, there is no solvent dependence for p-nitrophenylacetate ion which gives a carbanion with possibilities for more extensive delocalization. The magnitude of the variation is consistent with the known electrostrictive behavior of carboxylate ions. For example, the volume of ionization for a variety of carboxylic acids in water lies in a narrow range centered at −12 ml/mole as contrasted to values of −21 ml for the ionization of water and −28 ml for the ionization of amines.[12] The difference is owing to the fact that carboxylate ions have their charge equally divided between two oxygen atoms and consequently have weaker electric fields at their boundaries. The volumes of activation for the aqueous β-ketocarboxylates range from 2 to 5 ml/mole, and these can be accounted for by summing contributions of −10 ml for charge localization and 12–15 ml for bond stretching.

An interesting aspect of the results for trihaloacetate ions is the indication that charge localization increases in the sequence Br < Cl < F. This would seem to support the suggestion that trichloro- and tribromo-

(10) G. S. Hammond, *J. Am. Chem. Soc.*, 77, 334 (1955).
(11) J. Koskikallio and E. Whalley, *Can. J. Chem.*, 37, 788 (1959).

(12) S. D. Hamann, "Physico-Chemical Effects of Pressure," Butterworth and Co. (Publishers) Ltd., London, 1957, Section 7.ii.

methide ions carry part of their negative charge in the d orbitals of the halogen.[8]

Decarboxylation of Malonic and Related Acids. Transition states for the decomposition of β-keto acids are commonly supposed to result from redistribution of the electrons in the internally hydrogen-bonded form as follows.[13]
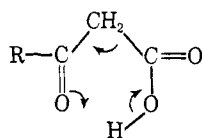
If the electronic shifts are synchronous, the transition state would have only a small dipole moment, but it is also conceivable that the molecule passes through a zwitterionic state as illustrated.[14]
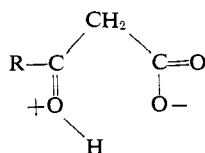
Westheimer[13] has argued against the dipolar structure on the grounds that polar solvents do not accelerate the reaction. On the other hand, the activation volumes for malonic acid favor the dipolar intermediate, since they decrease stepwise through a range of 14 ml as the polarity of the solvent is decreased in the sequence water, methyl sulfoxide, dioxan, tetrahydrofuran. Other reactions which produce polar products from nonpolar reactants show a similar variation;[2] for example, the activation volume for the reaction of n-butyl bromide with pyridine decreases by 16 ml on changing the solvent from aqueous alcohol to toluene. We believe that the variation of activation volume is more reliable than the variation of rate as a criterion of transition state polarization on the grounds that the physical basis is clearer and simpler. Indeed, the electrostriction is approximately calculable from a knowledge of the dielectric constant and its dependence on pressure.[15] On the other hand, the relation between free energy of activation and the degree of solvation is complicated by a multiplicity of contributing terms. In a previous confrontation of these criteria it was found that addition of water did not accelerate the ionogenic reaction of piperidine with halonaphthalenes and haloquinolines, whereas the activation volumes showed the expected variations.[16]

Dimethylmalonic acid and acetoacetic acid have nearly the same activation volume in water as malonic acid. Presumably, their transition states are similarly constituted.

Decarboxylation of Picolinic Acid. The currently accepted mechanism for the decomposition of picolinic acid is represented as follows.[8]
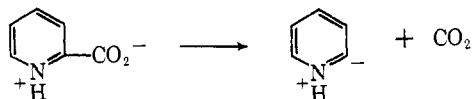
Figure 1. Sodium phenylpropiolate in water ($\triangle$); sodium phenylpropiolate in methanol (O); monosodium dimethylmalonate in water (∇); and dimethylmalonic acid in water ($\square$).

The high reactivity relative to that of benzoate ion is ascribed to the reduction of electrostatic potential as the charge centers converge during the activation process. The activation volumes in water (17 ml) and ethanol (19 ml) reinforce this hypothesis since their large magnitudes and their dependence on solvent polarity point to a release of solvent in the transition state. It should be noted, however, that the difference of 2 ml lies on the borderline of significance.

On the basis of ultraviolet spectroscopy it has been reported that picolinic acid is not zwitterionic in ethanol,[17] but the infrared absorption by carbonyl clearly indicates the opposite. By the method of attenuated total reflectance we find a maximum at 1575 cm^{-1} which agrees well with that of sodium acetate (1595 cm^{-1}) and differs from that of nonionized carboxylic acids (1700–1730 cm^{-1}).

Experimental Section

Apparatus. The high-pressure equipment, sampling technique, and general approach to measurement of rate constants have been described before.[2,18]

Errors. The mean deviation of duplicate rate measurements is usually about 3%. This corresponds to an error of 6% in ln (k_p/k_0) and 1 ml/mole in activation volume. Owing to the fact that we require fairly long reaction times it is not always possible to duplicate conditions used in previous kinetic studies; but where accurate thermodynamic constants of activation are available, as

(13) F. H. Westheimer and W. A. Jones, J. Am. Chem. Soc., 63, 3283 (1941); G. Fraenkel, R. L. Bedford, and P. E. Yankwich, ibid., 76, 15 (1954).
(14) K. J. Pederson, J. Phys. Chem., 36, 559 (1932).
(15) P. Drude and W. Nernst, Z. Physik. Chem., 15, 79 (1894).
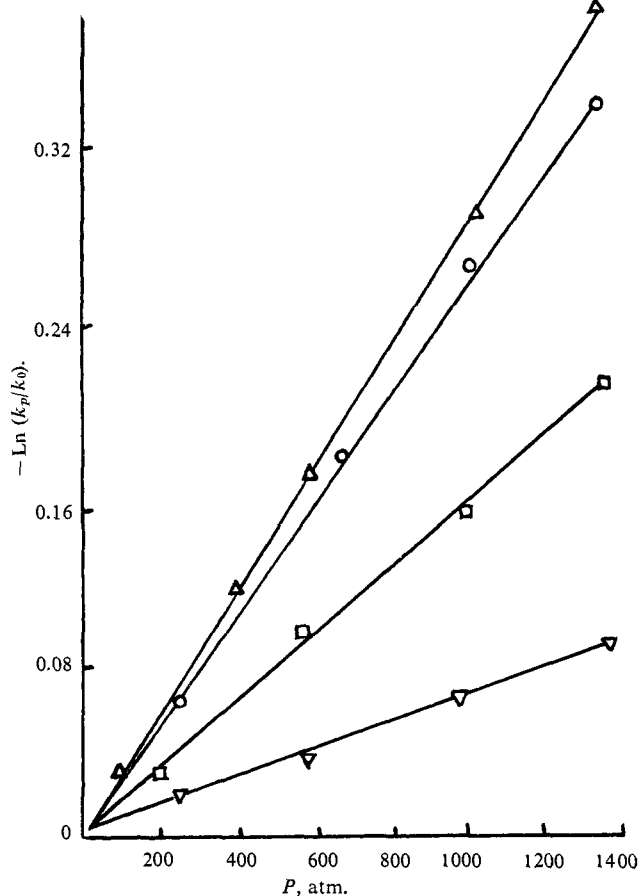(16) K. R. Brower, J. Am. Chem. Soc., 81, 3504 (1959).

(17) H. P. Stephenson and H. Sponer, ibid., 79, 2050 (1957); R. W. Green and H. K. Tong, ibid., 78, 4896 (1956).
(18) K. R. Brower, ibid., 80, 2105 (1958).

Table II. Summary of Kinetic Measurements

Methylmercuric fluoroborate (0.25 M) in water at 174.0°
$k_1{}^a$ = 0.635 k_{680} = 0.642 k_{1090} = 0.642 k_{1360} = 0.642

Ethylmercuric fluoroborate (0.25 M) in water at 114.0°
k_1 = 0.242 k_{1360} = 0.177

Isopropylmercuric fluoroborate (0.25 M) in water at 46.4°
k_1 = 0.573 k_{41} = 0.498 k_{680} = 0.484 k_{1090} = 0.386 k_{1360} = 0.355

Malonic acid (0.50 M) in water at 115.0°
k_1 = 0.363 k_{815} = 0.333 k_{1100} = 0.321 k_{1360} = 0.306

Malonic acid (0.50 M) in methyl sulfoxide at 81.3°
k_1 = 0.215 k_{272} = 0.215 k_{612} = 0.219 k_{1089} = 0.211 k_{1360} = 0.223

Malonic acid (0.50 M) in dioxan at 111.2°
k_1 = 0.119 k_{272} = 0.120 k_{612} = 0.136 k_{1089} = 0.156 k_{1360} = 0.163

Malonic acid (0.50 M) in tetrahydrofuran at 100.0°
k_{270} = 0.411 k_{600} = 0.465 k_{815} = 0.475 k_{1100} = 0.521 k_{1360} = 0.552

Dimethylmalonic acid (0.70 M) in water at 125.0°
k_{34} = 0.362 k_{270} = 0.353 k_{545} = 0.335 k_{815} = 0.327 k_{1360} = 0.299

Acetoacetic acid (0.50 M) in water at 40.0°
k_1 = 0.474 k_{270} = 0.453 k_{545} = 0.449 k_{815} = 0.422 k_{1360} = 0.385

Picolinic acid (0.60 M) in water at 180.0°
k_{55} = 0.204 k_{190} = 0.197 k_{408} = 0.174 k_{1090} = 0.133 k_{1360} = 0.112

Picolinic acid (0.60 M) in ethanol at 165.0°
k_{34} = 0.622 k_{270} = 0.565 k_{557} = 0.460 k_{940} = 0.396 k_{1360} = 0.313

Monosodium malonate (1.00 M) in water at 125.0°
k_{270} = 0.238 k_{600} = 0.277 k_{815} = 0.222 k_{1100} = 0.217 k_{1360} = 0.212

Monosodium dimethylmalonate (1.00 M) in water at 140.0°
k_{34} = 0.258 k_{272} = 0.252 k_{545} = 0.250 k_{815} = 0.245 k_{1360} = 0.239

Sodium benzoylacetace (1.00 M) in water at 54.4°
k_1 = 0.480 k_{270} = 0.455 k_{545} = 0.434 k_{815} = 0.405 k_{1360} = 0.361

Sodium dimethylacetoacetate (0.50 M) in water at 66.4°
k_{34} = 0.300 k_{353} = 0.279 k_{815} = 0.258 k_{1360} = 0.244

Sodium dimethylacetoacetate (0.50 M) in methanol at 45.0°
k_1 = 0.655 k_{815} = 0.691 k_{1360} = 0.775

Sodium phenylpropiolate (0.80 M) in water at 102.0°
k_{27} = 0.0873 k_{270} = 0.0764 k_{815} = 0.0673 k_{1360} = 0.0565

Sodium phenylpropiolate (0.50 M) in methanol at 102.0°
k_{27} = 0.117 k_{270} = 0.109 k_{815} = 0.095 k_{1360} = 0.081

Sodium p-nitrophenylacetate (0.58 M) in water at 129.0°
k_{27} = 0.114 k_{1080} = 0.073

Sodium p-nitrophenylacetate (0.50 M) in methanol at 114.4°
k_{27} = 0.195 k_{1360} = 0.128

Sodium trifluoroacetate (2.00 M) in water at 163.0°
k_{136} = 0.0453 k_{1360} = 0.0345

Sodium trifluoroacetate (0.96 M) in ethanol at 163.0°
k_{136} = 0.0486 k_{1360} = 0.0505

Sodium trichloroacetate (1.50 M) in water at 80.0°
k_{34} = 0.236 k_{270} = 0.212 k_{545} = 0.181 k_{1089} = 0.139 k_{1360} = 0.123

Sodium trichloroacetate (0.50 M) in ethanol at 60.5°
k_1 = 0.106 k_{1090} = 0.089

Sodium tribromoacetate (0.70 M) in water at 66.0°
k_1 = 0.114 k_{815} = 0.095 k_{1360} = 0.077

Sodium tribromoacetate (0.50 M) in ethanol at 30.4°
k_1 = 0.510 k_{1360} = 0.370

^{a} The symbol kp denotes the rate constant in hr^{-1} at p atmospheres.

for example those of malonic acid in water[13] or sodium phenylpropiolate in water,[19] our rates differ from the calculated rates by 5% or less. Temperatures were controlled within 0.05° and pressures within 7 atm. All proportional errors in the rate constants, such as those introduced by inert impurities in the starting materials, inaccurate standardizations, calibrations, etc., are canceled when the volume of activation is calculated.

Solvents. The ethanol was anhydrous, U.S.P. reagent quality, and the methanol was Van Waters and Rogers 99.8% grade. The dioxane and tetrahydrofuran were Eastman White Label grade and were purified by prolonged contact with sodium wire. The Eastman White Label methyl sulfoxide was used without further purification.

Acids. Malonic acids, picolinic acid, p-nitrophenylacetic acid, trifluoroacetic acid, and trichloroacetic acid were Eastman White Label grade. Dimethylmalonic acid, mp 190° dec, was prepared in 80% yield by saponification of the diethyl ester with 2 N sodium hydroxide under reflux for 4 hr. The diethyl ester, bp 102–103° (1 mm), was prepared in 61% yield by twice methylating malonic ester with equimolar amounts of sodium ethoxide and methyl iodide

in ethanol at room temperature. **Acetoacetic acid** was obtained in crude form in 10–20% yield by cold saponification of acetoacetic ester. The reaction mixture was acidified with sulfuric acid and extracted with ether which was then evaporated in the open air. The solutions used in the kinetic study were assayed for acetoacetic acid by complete decarboxylation. **Benzoylacetic acid**, mp 190° dec, was prepared in 50% yield by room-temperature saponification of ethyl benzoylacetate with 1.4 molar equiv of dilute sodium hydroxide. Addition of sulfuric acid precipitated the acid which was recrystallized from water. **Dimethylacetoacetic acid** was not isolated, but its sodium salt was obtained by room-temperature saponification of dimethylacetoacetic ester using the theoretical amount of 1 M sodium hydroxide in a mixture of 20% methanol and 80% water. The mixture was stirred until it became homogeneous. The solvent was removed by evaporation under vacuum without heating, and the concentration of solutions made from the residue was determined by complete decarboxylation. **Phenylpropiolic acid**, mp 136–138°, was prepared in 60% yield from cinnamic acid via the dibromide.[20] **Tribromoacetic acid**, mp 130–131°, was obtained in 50% yield by the reaction of bromal with 3.0

(19) R. A. Fairclough, *J. Chem. Soc.*, 1938, 1186.

(20) M. Reimer, *J. Am. Chem. Soc.*, **64**, 2510 (1942).

molar equiv of white fuming nitric acid at room temperature for 3 days. The crude product was purified by recrystallization from high-boiling ligroine. Recorded melting points for tribromoacetic acid are 131 and 135°. We were unable to obtain a melting point higher than 131° after several recrystallizations.

Sodium Carboxylates. Standardized solutions of sodium hydroxide in water, sodium methoxide in methanol, or sodium ethoxde in ethanol were used to neutralize weighed quantities of the acids, and the solutions were diluted to the required volume.

Alkylmercuric Halides. Methyl iodide, isopropyl bromide, and ethyl bromide were converted to Grignard reagents in anhydrous ether under 1 atm of hydrogen. The reaction mixture was filtered through glass wool into a flask containing a 25% molar excess of the corresponding mercuric halide, and the contents was stirred for 2 hr. The ether was allowed to evaporate, and the residue was recrystallized from alcohol. After several recrystallizations the yields ranged from 10 to 16%, and the melting points agreed with recorded values within 1°.

Alkylmercuric Fluoroborates. A standardized solution of silver fluoroborate was prepared by neutralizing a weighed amount of silver oxide with 50% fluoroboric acid. A weighed quantity of alkylmercuric halide (usually 6.25 mequiv) was added to a measured volume of silver fluoroborate (6.25 mequiv) amounting to about 10 ml, and the mixture was stirred for 1 hr. The aqueous layer would then give a negligible test for silver after oxidation with concentrated nitric acid and addition of chloride ion. After filtration of the metathesizing mixture, the filtrate and washings were diluted to 25 ml.

Reaction of Ethylmercuric Fluoroborate with Ethanol. When ethanol was substituted for water as a solvent it was observed that the decomposition produced a gas as well as metallic mercury. The sample cell was then fitted with a silicone rubber plug at the top for withdrawal of the gas by a hypodermic syringe. A 2-ml sample of 0.25 M ethylmercuric fluoroborate in ethanol was allowed to react to 91% completion at 120°, and the gas (about 1 ml under room conditions) was injected into a gas chromatograph which was fitted with a 12-ft column packed with hexadecane absorbent. The retention time was the same as that for the ethane peak of natural gas, and different from that of ethylene. In a synthetic mixture the ethane and ethylene peaks were resolved. A very rough estimate of the yield of ethane after allowing for the solubility in ethanol (~3 ml) is 30%.

The mercury droplet weighed 91.2 mg (calcd 91.0 mg).

The alcohol solution was added to a solution of 0.1 g of dinitrophenylhydrazine, 0.5 ml of sulfuric acid, and 0.7 ml of water in 2.0 ml of alcohol, and 27 mg (27%) of the dinitrophenylhydrazone of acetaldehyde, mp 147–148°, was obtained. A mixture melting point with an authentic sample was not depressed.

When a small portion of the alcohol solution was injected into the gas chromatograph, a peak with the same retention time as diethyl ether was obtained. The pulse height was the same as that of a solution of 0.36 ml of ether in 25 ml of ethanol which corresponds to 63% of theoretical according to the main solvolysis reaction

$$C_2H_5Hg^+ + C_2H_5OH \longrightarrow C_2H_6 + CH_3CHO + Hg + H^+$$

Analysis of Alkylmercuric Ion Solutions. To determine the concentration of unreacted alkylmercuric ion in connection with the rate measurements, we utilized the insolubility of alkylmercuric bromide. To the partly reacted solution was added a portion of standard potassium bromide solution equal to the initial RHg+ content, and the excess bromide ion concentration was determined by electrometric titration with silver nitrate solution using a silver electrode.

Volumetric Determination of Carbon Dioxide. The decarboxylation of malonic acid and its sodium salt in water, dimethylmalonic acid, and its sodium salt in water, and picolinic acid in water and ethanol was followed by direct measurement of the volume of carbon dioxide which collected above the solution in a glass bell. The technique was similar to one developed for the decomposition of diazonium ions.[1] The volume was corrected for the vapor pressure of solvent and the solubility of carbon dioxide in the liquid phase.

The decarboxylation of sodium benzoylacetate and sodium phenylpropiolate was followed by displacement of carbon dioxide with sulfuric acid within a mercury-filled gas buret. The buret was fitted with a stopcock and reservoir at the top by means of which the 1–2-ml sample was drawn inside together with 1 ml of rinse water. A 0.5-ml portion of 50% sulfuric acid liberated the carbon dioxide, and the measured volume was corrected for the vapor pressure of water and the solubility of carbon dioxide.

Titrimetric Determination of Carbon Dioxide. The decarboxylation of malonic acid in methyl sulfoxide, dioxane, and tetrahydrofuran was followed by titration of unreacted malonic acid with standard alkali after evaporation of solvent and acetic acid under vacuum at 70°. Analysis of synthetic mixtures gave results within 1% of theoretical.

The decarboxylation of the sodium trihaloacetates and sodium p-nitrophenyl acetate was followed by titration of the basic product, ethyl or methyl carbonate or bicarbonate ion, with standard hydrochloric acid. For the trichloro- and tribromoacetates it was found that mixtures reacted for both 10 and 20 half-lives gave 95–100% of the theoretical amount of base, and solvolysis of the haloform could therefore be safely neglected.

Determination of Activation Volume. From the data of Table II, values of ln (k_p/k_0) were computed and plotted against pressure as shown in Figure 1. A graphical determination of the slope gives $\Delta V^*/RT$.