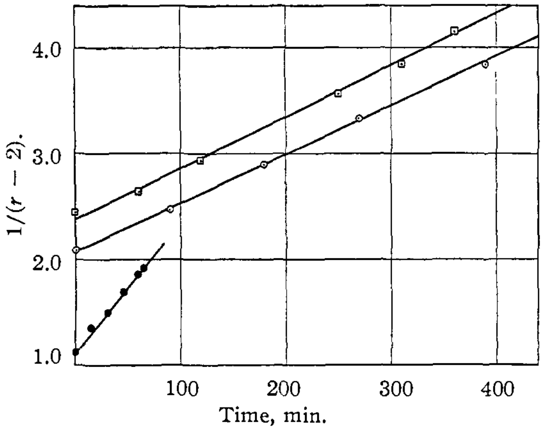

Fig. 9.—Reaction of saligenin with resorcinol at 99°: ●, run 10, 1 saligenin:1 resorcinol, no catalyst; ⊙, run 17, 1 saligenin:1 resorcinol:2 pinacol, no catalyst; ⊡, run 18, 1 saligenin:1 resorcinol:2 pinacol in the presence of triethanolamine.

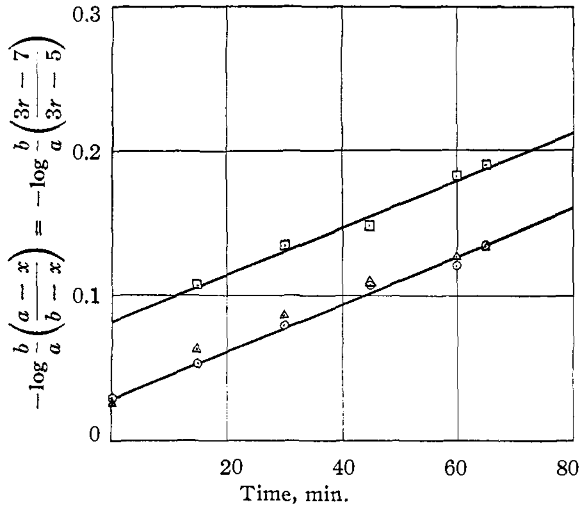

Fig. 10.—The reaction of saligenin with resorcinol at 99° and no catalyst: □, run 19, 1 saligenin:2 resorcinol:2 pinacol; O, run 21, 2 saligenin:1 resorcinol:2 pinacol; △, run 25, 1 saligenin:2 resorcinol:2 pinacol.

Summary

1. The condensation reactions of o-methylol phenol (saligenin) with itself, with phenol and with resorcinol have been studied in presence and absence of basic catalysts.

2. In absence of catalyst, 2,2'-dihydroxydibenzyl ether is formed from saligenin in high yield by an apparently second order reaction and with an activation energy of 20,000 cal./mole.

3. In presence of triethanolamine, sodium hydroxide, or a quaternary ammonium base, the self-condensation of saligenin obeys first order kinetics during about the first 50% of potential reactivity, after which departure from this relationship is observed. The final product is a resinous solid. The activation energy is 18,500 cal./mole. The specific rate constant is independent of basic strength or base concentration within the range studied.

4. The relationships of (2) and (3) are essentially unaltered when pinacol is used as diluent.

5. The reactions of saligenin with phenol and resorcinol are second order both in presence or absence of base or diluent. With resorcinol, the major product is a crystalline trihydroxydiphenylmethane. Weakly basic catalyst has no appreciable effect upon the reaction velocity.

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[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

The Acid-Catalyzed Decarboxylation of Cinnamic Acids

BY WILLIAM S. JOHNSON AND WALTER E. HEINZ

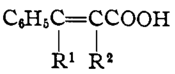
The experiments recorded herewith demonstrate that the decarboxylation of certain cinnamic acid types is promoted by mineral acid and that the rate of reaction is an increasing function of the concentration of the calayst. It appears, therefore, that the rate is influenced by the interaction of the catalyst with the organic acid, a conclusion which has profound bearing on the mechanism of the reaction and is particularly significant in view of the current feeling[1] that this is not a common type of behavior.

Experimental

The studies were carried out with the acids I-VI which, except for the last, were prepared *via* the Reformatsky reaction, followed by dehydration with formic acid and saponification according to general directions described elsewhere.[2] The decarboxylations were performed simply by boiling a solution of the organic acid in a mixture of 48% hydrobromic acid, acetic acid and water, the rate of reaction being determined by measurement of the volume of evolved carbon dioxide at appropriate intervals. The composition of the reagents (A–F) of various acid strength which were employed are given in Table I with the experimental data for calculation of the concentration of hydrobromic acid by volume. The description of the materials, apparatus and experimental procedure follows.

[1] *Cf.* (a) Schenkel and Klein, *Helv. Chim. Acta*, **28**, 1211 (1945); (b) Schenkel, *ibid.*, **29**, 436 (1946); (c) Shenkel and Shenkel-Rudin, *ibid.*, **31**, 514 (1948).

[2] Johnson and Glenn, THIS JOURNAL, **71**, 1087 (1949).



$$\underset{R^1}{C_6H_5C}=\underset{R^2}{C}COOH$$

I ($R^1 = C_6H_5$, $R^2 = H$)
II ($R^1 = CH_3$, $R^2 = H$)
III ($R^1 = C_2H_5$, $R^2 = H$)
IV ($R^1 = C_6H_5$, $R^2 = CH_3$)
V ($R^1 = H$, $R^2 = CH_3$)
VI ($R^1 = R^2 = H$)

The synthetic samples of organic acids which were employed in the decarboxylation studies had the following properties: β-phenylcinnamic acid (I), m. p. 161–162°, recrystallized from dilute alcohol[3]; β-methylcinnamic acid (II), m. p. 95–97°, recrystallized from 90–100° petroleum ether[4]; β-ethylcinnamic acid (III), m. p. 44–46°, recrystallized from 90–100° petroleum ether[5]; α-methyl-β-phenylcinnamic acid (IV), m. p. 159–162°, recrystallized from alcohol[6]; α-methylcinnamic acid (V), m. p. 82–83°, recrystallized from ether-petroleum ether.[7]

The apparatus consisted of a 50-ml. round-bottomed flask attached by a ground-glass joint to a small coil condenser which was connected to a three-way stopcock leading to the top of a 100-ml. mercury-filled gas buret. The flask was equipped with two side-arms, one bearing a thermometer (extending below the surface of the reaction mixture) and the other, a rod for puncturing the sample bulb (see below), held in place by a snugly-fitting rubber sleeve. Thin-walled sample tubes about 10 mm. in diameter were blown from capillary tubes formed by drawing 8-mm. soft glass tubing down to about 2 mm. in diameter. These tubes were filled through the neck with the powdered sample of organic acid and sealed off, the amount of the sample being obtained by difference in weights. These bulbs containing the samples were placed in the reaction flask along with 15 ml. of reagent (Table I) and a glass ebullition tube. The mixture was then heated in an oil-bath maintained at 140° with the system open to the atmosphere. After temperature equilibrium was reached the three-way cock was turned so as to engage the buret with the mercury level adjusted to zero. If after five minutes no volume or temperature changes were observed, the sample tube was ruptured, and gas readings were taken at appropriate time intervals (see Figs. 1, 2 and 3). The results of a typical experiment are recorded in Table II. No correction was made for the vapor pressure of the solvent which was relatively small at the temperature of the cooling system.

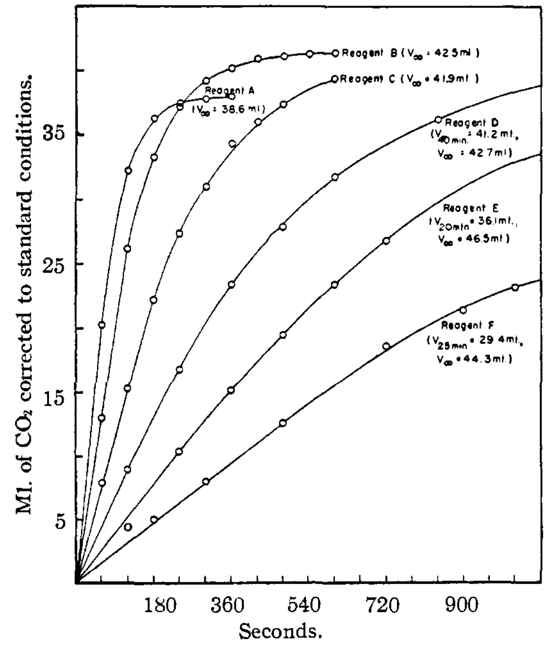


Fig. 1.—Decarboxylation of β-methylcinnamic acid (II) in reagents A–F.

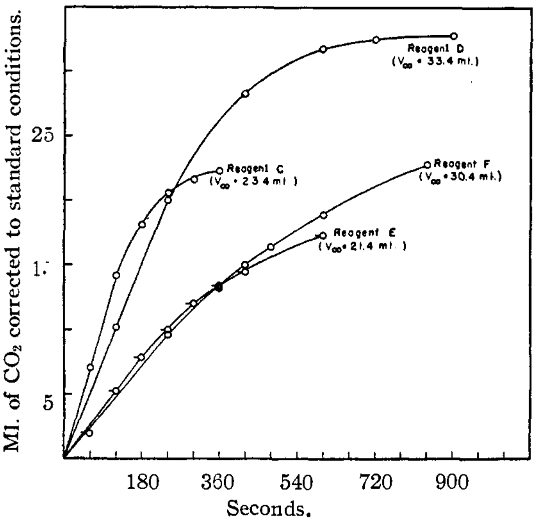


Fig. 2.—Decarboxylation of β-phenylcinnamic acid (I) in reagents C–F.

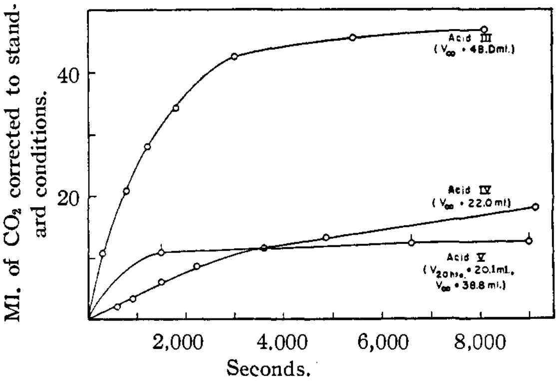


Fig. 3.—Decarboxylation of acids III, IV and V in reagent D.

The neutral product obtained by decarboxylation of 1.00 g. of α-methyl-β-phenylcinnamic acid by refluxing with 20 ml. of reagent A for one hour amounted to 0.80 g. (99% yield) of semi-crystalline oil which was principally 1,1-diphenylpropylene, $(C_6H_5)_2C{=}CHCH_3$. After distillation and recrystallization the m. p. was 47.5–48° (reported 48.5°[8] and 52°[9]).

The experimental data for most of the decarboxylations appear in Figs. 1, 2 and 3. The rates satisfied the requirements for first order kinetics with respect to the organic acid as shown by the sample calculation (Table II) of the specific rate constant for the decarboxylation of β-methyl-

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[3] *Cf.* Rupe and Busolt, *Ber.*, **40**, 4537 (1907).

[4] *Cf.* Lindenbaum, *ibid.*, **50**, 1270 (1917).

[5] *Cf.* Stoermer, Grimm and Laage, *ibid.*, **50**, 959 (1917).

[6] *Cf.* Rupe, Steiger and Fiedler, *ibid.*, **47**, 63 (1914).

[7] *Cf.* Dain, *J. Russ. Phys.-Chem. Soc.*, **28**, 593 (1896).

[8] Schorigin, *Ber.*, **41**, 2717 (1908).

[9] Klages, *ibid.*, **35**, 2646 (1902).

cinnamic acid (II) in reagent C, a straight-line relationship being obtained when the logarithm of the concentration is plotted against time (Fig. 4). The specific rate constants for each of the decarboxylations shown in Figs. 1, 2 and 3 are summarized in Table III.[10] For the sake of simplicity the rates were measured at the temperature of the boiling solvent at refluxing equilibrium conditions. This facilitated rapid dissolution of the organic acid as well as the maintenance of essentially adiabatic conditions. The comparison of k in solutions with different concentrations of mineral acid, however, is complicated by small variations in temperatures which invalidate any quantitative correlation of the rates with concentration of mineral acid. Such correlation would involve more precise studies at controlled temperature, as well as additional investigations to determine the acidity function of the reagents (see below). The present work is meant to demonstrate only the qualitative effect of acid concentration on the first-order rate constant. The behavior was most thoroughly studied with β-methylcinnamic acid (II), the rate constants k^{II} in each reagent (A-F) being recorded in column 3 of Table III. Although the reaction temperature with reagent A was only 7° higher than with F (representing the largest temperature discrepancy), the rate of decarboxylation of II in reagent A, designated k^{II}_{A}, was about 20 times greater than k^{II}_{F}. This effect is considerably beyond the expected limits of the influence of the temperature gradient.[11,12] Moreover, k^{II}_{E} which fortuitously was obtained at a temperature of 1° below k^{II}_{D}, nevertheless was four times the latter in magnitude. The steady decrease of k^{II} from the strongest reagent A to the weakest F, thus, constitutes proof of the thesis. Even allowing the highest limits of correction for variation of rate with temperature,

TABLE I

REAGENTS FOR DECARBOXYLATION EXPERIMENTS

Reagent	Vol. in ml. of 48% HBr[a]	CH₃COOH[b]	H₂O	Total vol., ml.	Concn. of HBr, moles/liter
A	12	8	4	23.6	4.5
B	10	10	5	24.5	3.6
C	6	9	4.5	19.2	2.7
D	5	10	5	19.6	2.2
E	4	12	6	21.4	1.6
F	3	12	6	20.5	1.3

[a] "Baker's Analyzed" reagent, J. T. Baker Chemical Co., sp. gr. 1.48–1.49. [b] Distilled from potassium permanganate.

TABLE II

DECARBOXYLATION OF 0.303 G. OF β-METHYLCINNAMIC ACID (II) IN REAGENT C AT 111°

Time, sec.	Vol. CO_2 obs.,[a] ml.	Vol. CO_2 at S. T. P., ml.	Concn. $(V_\infty - V)$, ml.	Log concn.	k (sec.$^{-1}$)
0	0	0	41.9	1.622	....
60	8.9	7.9	34.0	1.531	0.0035[b]
120	17.2	15.3	26.6	1.425	.0038[b]
180	25.0	22.2	19.7	1.295	.0042
240	30.7	27.3	14.6	1.164	.0044
300	34.8	31.0	10.9	1.037	.0045
360	38.5	34.2	7.7	0.886	.0047
420	40.5	36.0	5.9	.771	.0047
480	42.0	37.4	4.5	.653	.0046
600	44.3	39.4	2.5	.398	.0047
				Average k	.0045[c]

[a] At a pressure of 741 mm. and temperature of 26°. [b] This value is low apparently due to incomplete solution of organic acid, and was disregarded in calculation of average k. [c] The average deviation from this value is ±3.5%.

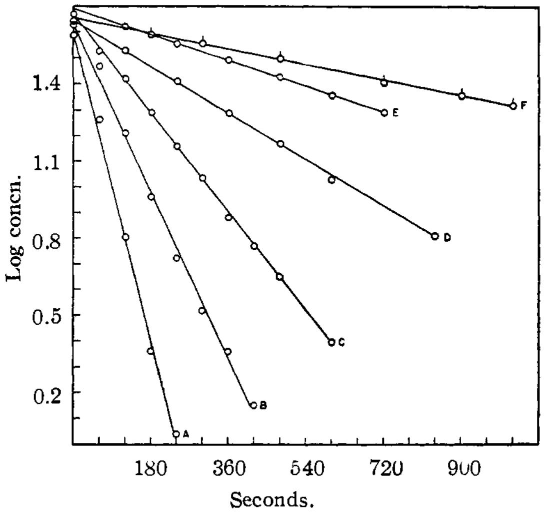

Fig. 4.—Decarboxylation of β-methylcinnamic acid (II) in reagents A–F.

TABLE III

AVERAGE SPECIFIC RATE CONSTANTS, k (SEC.$^{-1}$), FOR DECARBOXYLATION[10]

Reagent	Temp., °C.	Acids I	II	III	IV	V	VI
A	113	[a]	0.015				[d]
B	108	[a]	.0083				
C	111	0.0084	.0045				
D	109	.0046	.0022	0.00072	0.00020	[b]	[c]
E	107	.0027	.0011				
F	106	.0016	.00073				

[a] Rate of decarboxylation apparently was faster than rate of dissolution of organic acid. [b] Only 52% of calculated amount of gas was liberated after twenty hours, and rate did not appear to follow first-order kinetics; competing reaction was probably involved. [c] No apparent decarboxylation. [d] After forty-three hours only 26% of calculated amount of gas was evolved.

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[10] The average deviation from the average rate constant of I in reagent D (designated k^{I}_{D}) was ±8%. The average deviations from the average k of the other acids varied between ±5% (for k^{IV}_{D} and k^{II}_{A}) and ±0.7% (for k^{I}).

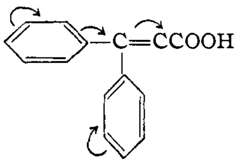
[11] "It is only very rarely that a homogeneous thermal reaction has a temperature coefficient greater than that obtained in the hydrolysis of cane sugar (k_{35}/k_{25} = 4.13)."

[12] Taylor, "A Treatise on Physical Chemistry," D. Van Nostrand Company, Inc., New York, N. Y., 1931, Vol. II, p. 970.

the first order rate constants for a given acid increase considerably more rapidly than defined by a straight line relationship of slope 1 with increasing concentration of hydrobromic acid. The deviation is particularly striking at the higher mineral acid concentrations, and suggests that in these media, the proton donating power or "acidity function,"[12] is significantly higher than the molarity of hydrobromic acid.

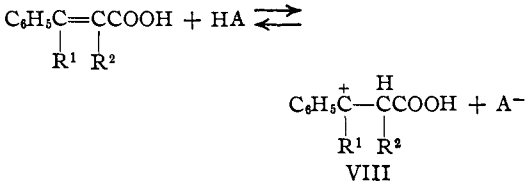
Theoretical Considerations[13]

The mechanism by which the acid catalyst promotes decarboxylation of the unsaturated acid $\underset{R^1}{C_6H_5C}{=}\underset{R^2}{C}COOH$ cannot be ascertained from the above data; however, it is reasonable to postulate the interaction of a proton with the organic acid. If H^+ makes an electrophilic attack at the α-carbon with concomitant rupture of the C–COOH bond, the mechanism would be bimolecular (S_E2) as suggested by Schenkel and Schenkel-Rudin[1c] for the decarboxylation of anthracene-9-carboxylic acid. The expected reactivity of the α-carbon toward such substitution may be measured in terms of its nucleophilic character as determined by the influence of the substituents on the α- and β-carbon atoms, and the observed relative order of rates of decarboxylation of acids I-VI in reagent D (Table III) are in essential agreement with this point of view. For example the relatively high rate of decarboxylation of β-phenylcinnamic acid (I) is attributable to the expectation that the β-phenyl groups would promote a center of high electron density at the α-carbon, *e. g.*

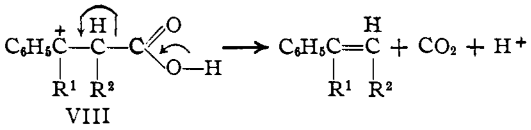


Groups attached to the benzene nuclei would accordingly be expected to exert an effect on the α-carbon predictable from Hammett's σ-constants as applied to the polarization of a simple ethylenic bond.[15]

Another method of predicting the influence of substituent groups is by a consideration of the transition-state, a contributing form of which is the carbonium ion $C_6H_5\underset{R^1}{\overset{+}{C}}-\underset{R^2}{\overset{H}{C}}COOH$. Obviously those substituents which tend to increase the susceptibility of the α-carbon to electrophilic attack, are those which have a corresponding "stabilizing" influence on the hypothetical carbonium ion, thus lowering the energy level of the transition-state. If such an ion does indeed have a true intermediary existence (and is not so highly stabilized that it will not collapse), it would be expected to decompose either by loss of a proton to regenerate the cinnamic acid or by rupture of the C–COOH bond to give the olefin. Moreover, the lower the energy-level of the transition-state, the more susceptible the acid would be to decarboxylation, provided of course that the transition-state is still unstable with respect to the products of the reaction.[16] This treatment suggests a more intimate and kineticly complex two-step mechanism involving (1) reversible reaction of the cinnamic acid with a proton donor to form an ionic intermediate, represented below in the form of the β-carbonium ion (VIII),[17] followed by (2) collapse of the ion VIII with rupture of the C–COOH bond which may be represented graphically in terms of the products of the reaction (equation 2). The actual mechanism of this decomposition, however, would probably not involve simultaneous rupture of the C–C and O–H bonds.

(1) 

$$\underset{R^1}{C_6H_5C}{=}\underset{R^2}{C}COOH + HA \rightleftarrows \underset{\text{VIII}}{C_6H_5\underset{R^1}{\overset{+}{C}}-\underset{R^2}{\overset{H}{C}}COOH} + A^-$$

(2) 

$$\underset{\text{VIII}}{C_6H_5\underset{R^1}{\overset{+}{C}}-\underset{R^2}{\overset{\boxed{H}}{C}}-C\begin{matrix}{\scriptstyle //O}\\ {\scriptstyle \backslash O-H}\end{matrix}} \longrightarrow \underset{R^1}{C_6H_5C}{=}\underset{R^2}{\overset{H}{C}} + CO_2 + H^+$$

The relative rates of decarboxylation of the acids I-VI in reagent D (Table III) are treated below according to such a scheme, with full realization that there is no evidence that the β-carbonium ion or other contributing forms has a real existence. We hope to shed some light on this question by a study of the quantitative effect of concentration of catalyst on the rate, and by examination of the decarboxylation of *cis*- and *trans*-forms of substituted cinnamic acids. Retention of configuration by the olefins produced would be incompatible with the β-carbonium ion theory.

Of the acids I-VI, β-phenylcinnamic acid (I) would be expected to decarboxylate most rapidly, since it provides the carbonium ion of lowest energy level due to the contribution of 6 reso-

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(13) Hammett, "Physical Organic Chemistry," McGraw-Hill Book Company, New York, N. Y., 1940, p. 267.

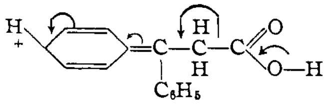
(14) In a discussion of this manuscript with Professor P. D. Bartlett on December 23, 1948, we learned that he was initiating a study to support a similar but independently conceived view regarding the acid-catalyzed decarboxylation of certain acids.

(15) *Cf.* Bergmann and Szmuszkowicz, THIS JOURNAL, **70**, 2748 (1948).

(16) A similar argument has been employed recently by Waters, *J. Chem. Soc.*, 727 (1948), to explain the course of aromatic substitution reactions

(17) The formation of such an ion can be envisaged also as proceeding *via* a 1,4-mechanism involving initial attack of the proton on an oxygen atom of the carboxyl group, followed by a prototropic shift.

nance forms like IX (in addition to VIII) to the electronic state of the ion. The decarboxylation of the ion may be pictured as well from any one of these canonical forms (see arrows, formula IX) with the reservations mentioned above.

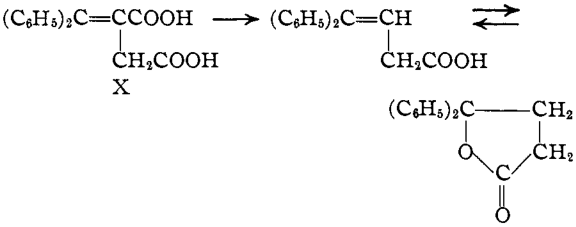

IX

When R^1 = alkyl instead of phenyl the rate of decarboxylation diminishes because this influence of one of the β-phenyl groups is lost. However, compared to hydrogen the positive inductive effect of the β-alkyl group would be expected to lower the energy level of the ion (*cf.* the stability of *t*-alkyl carbonium ions over other alkyl carbonium ions), which is consistent with the fact that II decarboxylates more rapidly than VI. The more rapid decarboxylation of II than III suggests that the β-methyl substituent leads to a carbonium ion of lower energy level than does the β-ethyl group. If this is due to a hyperconjugation effect, then the rate of decarboxylation would be lower yet with β-isopropyl- and even lower with β-*t*-butylcinnamic acid.

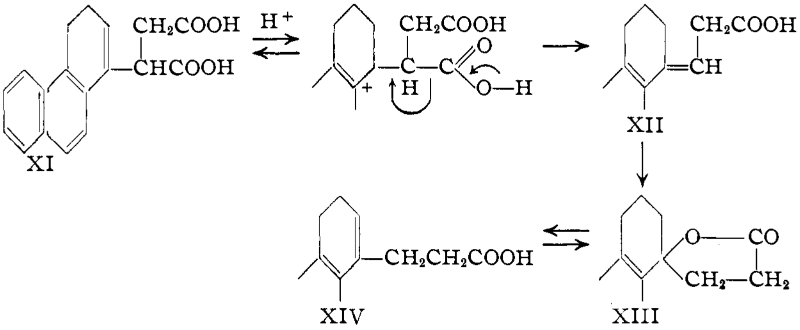
The slow decarboxylation of the parent compound (VI) is expected since there is only one instead of two +I β-substituents. It is expected that a β-alkyl-α,β-unsaturated acid, RCH=CH₂COOH, would be even less susceptible to acid-catalyzed decarboxylation, and that acrylic acid derivatives with no β-substituent would be the least susceptible of the group.

Introduction of an α-methyl substituent in place of the hydrogen of β-phenylcinnamic acid significantly decreased the rate of decarboxylation, k_D^{IV} being 1/23 of k_D^{I}. This is the expected behavior, since the polarizing influence of the α-methyl substituent on the ethylenic bond is in a direction opposite to that required for production of the β-carbonium ion. In addition an α-substituent could conceivably afford steric hindrance to the approach of the proton ("B" Strain). Although a similar substituent in cinnamic acid appears to increase the rate, this situation is not comparable, since the decarboxylation of V and VI was incomplete and did not follow first order kinetics, suggesting that competing reactions (such as cyclization) were involved.

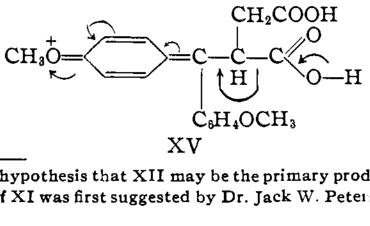
The decarboxylation of certain itaconic acids has been shown to be acid-catalyzed,[18] and the β-carbonium ion mechanism provides a means of predicting the behavior. For example, the decarboxylation of diphenylitaconic acid (X) to give an equilibrium mixture of γ,γ-diphenylvinylacetic acid and γ,γ-diphenylbutyrolactone, may be considered a special case of the cinnamic acid decarboxylation (equations 1 and 2) where R^1 = C_6H_5 and R^2 = CH_2COOH. The unsaturated acid, thus, would be the primary product of decarboxylation and the former postulation of an intermediary paraconic acid[18] is indefensible.



In the dihydrophenanthrylsuccinic acid (XI) studies, it was discovered that the rate of decarboxylation was greater than the rate of equilibration of the lactone XIII with the unsaturated acid XIV, thus it was possible to isolate a mixture containing a higher proportion of XIII than exists at equilibrium. This observation means that the lactone XIII is the precursor of the γ,δ-unsaturated acid XIV. The primary product of decarboxylation may indeed be the expected β,γ-unsaturated acid XII which is not isolated because of rapid lactonization XII → XIII.[19]



According to the β-carbonium ion treatment, methoxyl groups in the ortho- and para-position of the phenyl group of cinnamic acids would be expected to promote the acid-catalyzed decarboxylation. The examination of this behavior is in progress. It has been noted for example that *p,p'*-dimethoxydiphenylitaconic acid is extraordinarily susceptible to decarboxylation (decomposing slowly even in warm aqueous acid) presumably due to the contribution of ionic forms like XV the decomposition of which may be represented graphically by the indicated electronic shift.


XV

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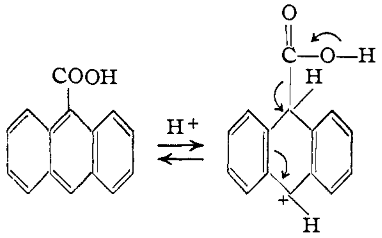
[18] Johnson, Petersen and Schneider, THIS JOURNAL, **69**, 74 (1947).

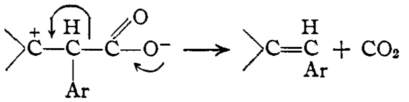
[19] The hypothesis that XII may be the primary product of decarboxylation of XI was first suggested by Dr. Jack W. Petersen in 1945.

The acid-catalyzed decarboxylation of anthracene-9-carboxylic acid XVI,[1b] may also be treated by the β-carbonium ion mechanism. The relationship of the ionic form XVII to the relatively stable benzhydril carbonium ion suggests that the energy level of the transition-state would be correspondingly low, and leads to the prediction that the acid would be relatively susceptible to decarboxylation.



XVI XVII

The formation of olefins by loss of carbon dioxide in the Meerwein reaction can be treated similarly from the postulated intermediate $>\overset{+}{C}$—CHArCOO$^-$,[20] *viz.*



It is equally plausible to envisage the decarboxylation as proceeding through the acid $>\overset{+}{C}$—CHAr-COOH, but in any event the postulation of a β-lactone intermediate[20] seems unnecessary.

In other experiments which will be described in a future communication it will be shown that the well-known decarboxylation of paraconic acids is probably acid-catalyzed and can be treated satisfactorily by the β-carbonium ion theory.

Acknowledgment.—We are deeply grateful to Dr. Gilbert Stork for inquiring discussions which afforded much of the stimulation for the initiation of this work, and to Drs. P. D. Bartlett and S. Winstein for helpful criticisms relating to the theoretical considerations.

Summary

It has been demonstrated that certain α,β-unsaturated acids of the cinnamic acid type will undergo a truly acid-catalyzed decarboxylation, and that the rates are dependent upon the concentration of catalyst. The relative rates of decarboxylation of variously substituted unsaturated acids have been examined, and the mechanism is discussed.

MADISON, WISCONSIN RECEIVED JANUARY 15, 1949

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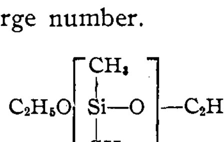
[20] Meerwein, Büchner and Emster, *J. prakt. Chem.*, **152**, 237 (1939).

[CONTRIBUTION FROM THE DOW CORNING CORPORATION]

Organosilicon Polymers. V. Linear Dimethylsiloxanes with Ethoxyl End-Groups

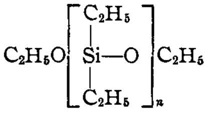
BY H. J. FLETCHER AND M. J. HUNTER

In recent papers[1,2,3] the preparation and properties of several series of low polymer dimethylsiloxanes have been described. This paper is a continuation of the work carried out by this group and will describe the series of open-chain dimethylsiloxanes[4] with ethoxyl end-groups represented by formula I where *n* may vary from 1 to a very large number.



$$C_2H_5O\left[\begin{array}{c}CH_3\\|\\Si-O\\|\\CH_3\end{array}\right]_n-C_2H_5 \qquad I$$

Andrianov[5] described a mechanism for the hydrolysis and condensation of dialkyldiethoxysilanes and has given data on the series represented by formula II where *n* varies from 1 to 10.



$$C_2H_5O\left[\begin{array}{c}C_2H_5\\|\\Si-O\\|\\C_2H_5\end{array}\right]_nC_2H_5 \qquad II$$

The methylpolysiloxanes of formula I may be prepared by partially hydrolyzing diethoxydimethylsilane.[6] The condensation products from this reaction will have a molecular weight dependent upon the quantity of water used.

When hydrolysis was carried out with 0.75 mole of water per mole of diethoxydimethylsilane a series of polymers was obtained which were separated on fractional distillation as progressively higher boiling plateaus. The first plateau, after the removal of the alcohol formed, was unreacted diethoxydimethylsilane, and subsequent plateaus were the succeeding members of the series. Analyses and physical properties of the redistilled compounds are given in Table I. Data on diethoxydimethylsilane are included for the sake of comparison.

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[1] Hunter, Hyde, Warrick and Fletcher, THIS JOURNAL, **68**, 667 (1946).

[2] Patnode and Wilcock, *ibid.*, **68**, 358 (1946).

[3] Hunter, Warrick, Hyde and Currie, *ibid.*, **68**, 2284 (1946).

[4] U. S. Patent 2,415,389, February 4, 1947, by Hunter, Fletcher and Currie.

[5] Andrianov, *J. Gen. Chem., U. S. S. R.*, **16**, 633–638 (1946).

[6] (a) U. S. Patent 2,380,057, July 10, 1945, by McGregor and Warrick; (b) U. S. Patent 2,384,384, September 4, 1945, by McGregor and Warrick.