cyanate. The copper salt of 2-mercaptoethyl thiocyanate[13] was made by the reaction of the copper salt of acetoacetic ester with ethylene dithiocyanate in absolute ethanol. Trimethylene dithiocyanate[4] was prepared from trimethylene dibromide and potassium thiocyanate. 2-Mercaptoethyl acetate,[14] b.p. 62–66° (16 mm.), was made from 2-mercaptoethanol and acetic anhydride. Cysteine hydrochloride, 1,2-dimercaptoethane and 2-mercaptoethanol were commercial materials.

Tests for Thiocyanate Ion Evolution. (a) Mercaptans.—A small volume (about 3 ml.) of redistilled cyanogen chloride was added to a solution of about 0.1 g. of the substance to be tested in 2–3 ml. of water or ethanol–water. After a few minutes, the solution was made alkaline by the addition of aqueous sodium hydroxide (with care, in the case of cysteine hydrochloride, to raise the *p*H above 9). On acidification of the mixture and addition of a few drops of 5–30% aqueous ferric chloride solution, a deep red color indicated the presence of thiocyanate ions. Positive tests were obtained with 1,2-dimercaptoethane and cysteine hydrochloride, and a negative test with 2-mercaptoethanol.

(b) **Organic Thiocyanates and 2-Imino-1,3-dithiolane.**—The previously described procedure was followed with omission of the cyanogen chloride. Positive tests were obtained with ethylene dithiocyanate, methylene dithiocyanate, the copper salt of 2-mercaptoethyl thiocyanate and 2-imino-1,3-dithiolane, and a negative test with trimethylene dithiocyanate.

Identification of the Products of Reaction of Ethylene Dithiocyanate with Base. (a) In Aqueous Ethanol.—Ethylene dithiocyanate (0.1 g.) was dissolved in 25 ml. of 95% ethanol. Two milliliters of 0.2 *N* sodium hydroxide was added and the solution was allowed to stand two hours, after which 1 ml. of 6 *M* sulfuric acid was introduced. After addition of 20 ml. of water to the mixture, the precipitate was filtered off, dissolved in hot N,N-dimethylformamide and decolorized with a small amount of charcoal and diatomaceous filter aid. After filtration to remove the decolorizing agents, water was added until the hot solution became slightly cloudy. As the solution cooled, a precipitate formed which was reprecipitated in the same manner several times, until a constant melting point of 105–107° had been obtained. This substance gave an analysis close to that calculated for ethylene sulfide polymer. *Anal.* Calcd. for $(C_2H_4S)_x$: C, 40.0; H, 6.7; S, 53.3. Found: C, 39.4; H, 6.3; S, 53.1.

An authentic sample of ethylene sulfide polymer[14] was made by dissolving 1 g. of 2-mercaptoethyl acetate in 5 ml. of absolute ethanol and adding 3 ml. of 20% sodium hydroxide. After one hour, a few ml. of water was added and the mixture was filtered. The solid thus obtained was precipitated several times from solution in N,N-dimethylformamide, as described in the preceding paragraph, and finally washed with ethanol and ether, m.p. 108–109°.

(b) **In Aqueous Acetone.**—Ethylene dithiocyanate (0.5 g.) was dissolved in 3 ml. of acetone. Three milliliters of 20% aqueous sodium hydroxide was added, the mixture was shaken well and 20 ml. of water was stirred in. After 15 minutes, the oily globules of ethylene sulfide that had formed were extracted with ether and the aqueous layer was separated and treated with 0.5 g. of semicarbazide hydrochloride in saturated aqueous solution. The *p*H was reduced to 8 by dropwise addition of dilute hydrochloric acid and the solution was permitted to stand several hours. The precipitate of hydrazodicarbonamide, a standard derivative for cyanate,[15] was isolated by filtration and air-dried, m.p. 253–256°, literature[16] m.p. 254–259°.

Acknowledgment.—The authors are pleased to acknowledge the interest and encouragement of Dr. Albert A. Kondritzer, who made it possible for this work to be carried out.

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[13] E. P. Kohler, *Am. Chem. J.*, **22**, 67 (1899).

[14] L. W. C. Miles and L. N. Owen, *J. Chem. Soc.*, 817 (1952).

[15] F. J. Welcher, "Organic Analytical Reagents," Vol. II, D. Van Nostrand Co., Inc., New York, N. Y., 1947, p. 454.

[16] N. A. Lange, "Handbook of Chemistry," 8th ed., Handbook Publishers, Inc., Sandusky, Ohio, 1952, p. 558.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WASHINGTON]

General *vs.* Specific Acid–Base Catalysis in Strong Mineral Acid Solution. Aromatic Decarbonylation[1]

BY W. M. SCHUBERT AND PHILIP C. MYHRE[2]

RECEIVED NOVEMBER 9, 1957

Isotope effects have been determined for the decarbonylation of 2,4,6-triisopropylbenzaldehyde in 71–99% D_2SO_4–D_2O and for 2,4,6-triisopropylbenzaldehyde-d_1 (ArCDO) in 72–96% H_2SO_4–H_2O. The results are in complete agreement with the general acid–base catalysis mechanism of successive bimolecular proton transfer steps previously proposed. In accordance with expectation, based on steric grounds, a step involving proton transfer from solvent acids to the aromatic ring is rate controlling in the higher H_2SO_4 percentages and largely rate controlling in the lower H_2SO_4 percentages. Conclusions of general significance are: (1) general acid–base catalysis in non-dilute H_2SO_4 has been demonstrated; (2) agreement with the Hammett acid catalysis equation, $\log k_{\text{obsd}} + H_0 - \log ([\text{B}]/[\text{B}]_{\text{stoich}}) = \text{constant}$, over a limited acid range, is not a sufficient criterion for the assignment of mechanism; (3) the mechanism of successive bimolecular proton transfer steps assigned to the decarbonylation may give agreement with the Hammett equation under the condition that acid and/or basic catalysis constant ratios are the same as for indicator bases; (4) additional evidence that aromatic electrophilic substitution in general proceeds *via* an intermediate has been obtained.

The following bimolecular mechanism has been proposed for the replacement of the formyl group by hydrogen that occurs when 2,4,6-trialkylbenzaldehydes are treated with strong mineral acid (*e.g.*, 60–100% H_2SO_4).[3,4]

In these equations, HA_i refers to solvent acids (*i.e.*, $H_3O^{\oplus}$ and H_2SO_4) and A_i refers to solvent bases (*i.e.*, H_2O and $HSO_4^{\ominus}$), with the charges unspecified. This mechanism was found to be consistent with all of the experimental facts amassed including the changes in k_{obsd} with percentage sulfuric acid for 2,4,6-trimethyl-, triethyl- and triisopropylbenzaldehyde, and the isotope effects for deuteromesitaldehyde (MesCDO) in 60–100% D_2SO_4–D_2O.[4] Disagreement with the experimental facts was found for each of a number of other mechanisms considered, including the general Hammett mechanism and termolecular mechanisms.

In terms of this mechanism, the observed deuterium isotope effects with deuteromesitaldehyde

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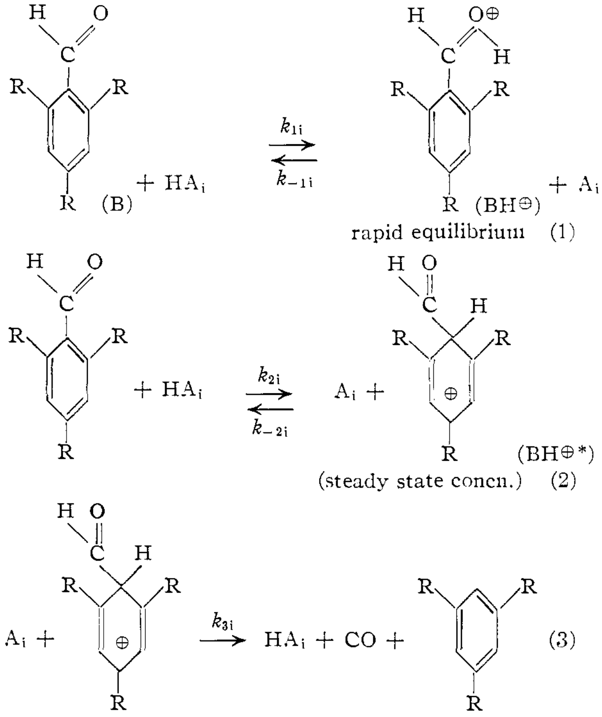
[1] Presented at the Symposium on Aromatic Substitution, 130th National Meeting of the American Chemical Society, Atlantic City, N. J., September, 1956.

[2] Du Pont Pre-doctoral Fellow, 1956–1957.

[3] W. M. Schubert and R. E. Zahler, THIS JOURNAL, **76**, 1 (1954).

[4] W. M. Schubert and H. Burkett, *ibid.*, **78**, 64 (1956).

(MesCDO) in sulfuric acid solutions and with mesitaldehyde in deuterosulfuric acid solutions require that in low mineral acid concentrations (59–70% H_2SO_4) step 3 be rate-controlling and step 2 be an established equilibrium, whereas in high acid concentrations (85–100% H_2SO_4) steps 3 and 2 forward be competing rate controlling steps of comparable magnitude.[4] This means that in the lower H_2SO_4 concentrations, v_{-2} is appreciably greater than v_3 (where v is velocity) and in the higher H_2SO_4 concentrations, v_{-2} is comparable to v_3.



Such a slowdown with increasing H_2SO_4 concentration of step 2 reverse relative to step 3 was rationalized as follows: Both 2 reverse and 3 involve proton abstraction from the same species, $BH^{*\oplus}$, by solvent bases. However, the proton being abstracted in 2 reverse lies at a different site than the one being abstracted in step 3; therefore, there is no *per se* reason to expect the relative catalytic effectiveness of $HSO_4^{\ominus}$ to that of H_2O to be the same in the two steps (see *e.g.*, references 5 and 6). Provided that $k_{-2\text{H}_2\text{O}}/k_{3\text{H}_2\text{O}}$ is sufficiently greater than unity and $k_{-2\text{HSO}_4^{\ominus}}/k_{3\text{HSO}_4^{\ominus}}$ has a value around unity or less (and presuming $k_{\text{H}_2\text{O}} > k_{\text{HSO}_4^{\ominus}}$) then it should be found that: (1) in the low mineral acid percentages (59–70% H_2SO_4), in which the concentration of water exceeds that of bisulfate ion, step 2 should be an established equilibrium and step 3 rate controlling; (2) in the high acid percentages (85–100% H_2SO_4), in which the population of bisulfate ion greatly exceeds that of water, step 2 reverse should be slowed relative to 3 and, consequently, 2 forward could then become partially rate-controlling in competition with 3.[4]

A reduction in the catalytic effectiveness of bisulfate ion (relative to water) in step 2 reverse (compared to step 3) may be due, at least in part, to steric factors [4] That is, there may be a greater increase in steric strain in step 2 reverse than in step 3 with the bulkier bisulfate ion; *i.e.*, the proton being abstracted in step 2 reverse lies at a considerably more hindered position than the proton being abstracted in step 3. If such a steric factor plays a role in reducing the relative effectiveness of bisulfate ion in step 2 reverse for mesitaldehyde, then it would be expected that the relative effectiveness of bisulfate ion would be reduced even further in step 2 reverse for 2,4,6-triisopropylbenzaldehyde. This should result in a further slowdown of step 2 reverse relative to step 3 in the high acid percentages, perhaps enough to make step 2 forward largely rate controlling. Furthermore a very large reduction in the relative catalytic effectiveness of bisulfate ion in step 2 reverse would impart a behavior approaching specific oxonium ion catalysis to the decarbonylation of 2,4,6-triisopropylbenzaldehyde. We have studied the decarbonylation of 2,4,6-triisopropylbenzaldehyde-d_1 (ArCDO) in 72–96% H_2SO_4, and of the ordinary aldehyde in 71–99% D_2SO_4–D_2O in order to determine whether these expectations could be realized.

Experimental

2,4,6-Triisopropylbenzaldehyde-d_1.—The method used in the preparation of mesitaldehyde-d_1 was applied to the preparation of 2,4,6-triisopropylbenzaldehyde-d_1 (ArCDO).[4] The isotopic purity of the aldehyde was checked by infrared analysis. To obtain maximum resolution of the spectrum, a special spectrophotometer equipped with a calcium fluoride prism was used.[7] A comparison of the aldehydic C–D (4.75, 4.85μ) and C–H (*ca.* 3.5, 3.6μ) stretching bands indicated that the aldehyde was at least 90% ArCDO.

The preparation of other materials is described in previous publications.[3,4]

Kinetic Method.—The spectrophotometric method for determining the first-order rate constants, using a Beckman DU instrument fitted with a constant temperature bath, has been described previously.[3] The temperature was controlled to ±0.05°.

Results

Basicity Determinations.—The ultraviolet spectrum, at room temperature, of 2,4,6-triisopropylbenzaldehyde-d_1 was identical to that of the ordinary aldehyde in several percentages of sulfuric acid, including 64.4%, in which the amounts of free base and oxygen conjugate acid of the substrate are about the same. Therefore, the ordinary and deuteroaldehyde have experimentally identical basicity.

The extent of conjugate acid formation of 2,4,6-triisopropylbenzaldehyde in D_2SO_4–D_2O *vs.* that in the corresponding percentage sulfuric acid was determined spectrophotometrically at room temperature, as was done for mesitaldehyde.[4] It was found that conjugate acid formation is more nearly complete in D_2SO_4. The value of $H_0(H_2SO_4) - H_0(D_2SO_4)$ using triisopropylbenzaldehyde as the indicator base was found to be 0.3 in the region of 65.1% H_2SO_4. This compares with the value of 0.35 found for mesitaldehyde in 59–70% acid.[4] The greater "acidity" of deuterosulfuric acid as against sulfuric acid is illustrated in Fig. 1.

Rate Results.—For the determination of the first-order rate constants the plot of $\log (D - D_\infty)$ *vs.*

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(5) L. Zucker and L. P. Hammett, THIS JOURNAL, **61**, 2785 (1939).

(6) R. P. Bell, "Acid–Base Catalysis," Oxford University Press, London, 1941, Chapter VII.

(7) We wish to thank Dr. David F. Eggers, Jr., for the use of his apparatus and his help in interpreting the results.

time was linear within ±0.05 of log $(D - D_\infty)$. The plot was made for at least two wave lengths in each separate run. The reaction was followed in all runs to 75–90% completion. The maximum deviation was ±4% and the average deviation was ±2%. The rate constants obtained are given in Tables I and II.

TABLE I

FIRST-ORDER RATE CONSTANTS FOR THE DECARBONYLATION OF 2,4,6-TRIISOPROPYLBENZYLALDEHYDE AND 2,4,6-TRIISOPROPYLBENZALDEHYDE-d_1 IN H_2SO_4 AT 80°

H_2SO_4, %	$k_{obsd} \times 10^3$ sec.$^{-1}$ ArCHO	ArCDO	k_{ArCHO}/k_{ArCDO}
96.8	1.32, 1.29	1.31, 1.29	1.01
93.4	2.00, 2.02	1.87	1.07
90.9	2.30	2.20	1.04
90.9[a]	0.558[a]	0.542[a]	1.03
89.8	2.36, 2.30	2.29, 2.36	1.01
84.9	3.24[b]	2.45	1.32
79.0	3.60[b]	2.83, 2.81, 2.82	1.27
77.4	3.45[b]	2.93	1.18
72.5	2.70[b]	2.12	1.27

[a] D_2SO_4–D_2O. [b] Previously reported.[3]

TABLE II

FIRST-ORDER RATE CONSTANTS FOR THE DECARBONYLATION OF 2,4,6-TRIISOPROPYLBENZALDEHYDE IN D_2SO_4–D_2O AND IN H_2SO_4 AT 80°

Acid, %	$k_{obsd} \times 10^3$ sec.$^{-1}$ D_2SO_4	H_2SO_4	$\frac{k_{H_2SO_4}}{k_{D_2SO_4}}$	$\frac{[B] \text{ in } H_2SO_4}{[B] \text{ in } D_2SO_4}$
99.0	0.146	0.723	5.0	2.0
95.5	.306	1.51	4.9	2.0
93.5	.478	2.00, 2.02	4.2	2.0
90.9	.558	2.30	4.1	2.0
90.9[a]	.542[a]	2.20[a]	4.1[a]	2.0[a]
86.6	.772	3.05[b]	4.0	2.0
80.0	.952	3.70[b]	3.9	2.0
70.7	.752	2.33[b]	3.2	1.6[c]

[a] These runs made on 2,4,6-triisopropylbenzaldehyde-d (ArCDO). [b] Previously reported.[3] [c] Assumes the degree of oxygen conjugate acid formation to be the same at 80° as at room temperature.

Discussion

The general rate expression for the mechanism assigned (equations 1, 2 and 3) is given by equation 4.

$$k_{obsd} = \frac{[B]}{[B]_{stoich}} \frac{\Sigma k_{2i}[HA_i]f_B f_{HAi}/f_{tr_{2i}}}{1 + \frac{\Sigma k_{-2i}[A_i]f_{Ai}/f_{tr_{2i}}}{\Sigma k_{3i}[A_i]f_{Ai}/f_{tr_{3i}}}} \quad (4)$$

Equation 4 is derived assuming only that the carbon conjugate acid, $BH^{*\oplus}$, is in steady state concentration.[4] This equation applies when either step 3 or step 2 forward is rate controlling, or when both are rate controlling, although it may be simplified in the former instances.[4–6] Equilibrium 1 is established instantly and the extent of it is readily measured.[8a] It plays no direct role in the processes leading to the decarbonylation products, but acts only to reduce the concentration of B, the reactive substrate species in step 2.

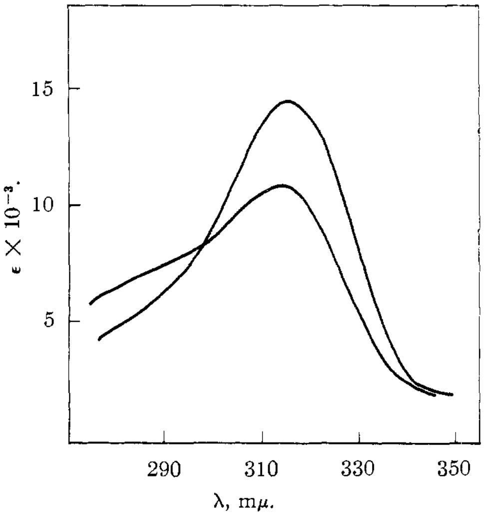

Fig. 1.—Spectrum of 2,4,6-triisopropylbenzaldehyde: upper curve, in 65.1% D_2SO_4–D_2O; lower curve, in 65.1% H_2SO_4.

Examination of the rate data of Table I reveals that in the higher sulfuric acid percentages (>85%) the ratio of observed rate constants, k_{ArCHO}/k_{ArCDO}, is practically unity; *i.e.*, there is practically no isotope effect for the decarbonylation of 2,4,6-triisopropylbenzaldehyde-d_1. Table II reveals that the decarbonylation of the hydrogen aldehyde proceeds at a considerably slower rate in D_2SO_4–D_2O solutions than in corresponding percentages of H_2SO_4.[8b] The maximum in $k_{H_2SO_4}/k_{D_2SO_4}$ is 5.0, in 99% acid, and declines slowly as the mineral acid percentage is decreased. The k_{ArCHO}/k_{ArCDO} ratio of unity in greater than 85% H_2SO_4 indicates that a step involving cleavage of the aldehydic C–H (or C–D) bond (*i.e.*, step 3) is not detectably rate controlling. The large $k_{H_2SO_4}/k_{D_2SO_4}$ ratio indicates that a step involving proton transfer from solvent acids (*i.e.*, step 2) is at least partially rate-controlling. The two results taken together, then, lead to the conclusion that in the higher percentages of mineral acid (>85%), step 2 forward is practically completely rate-controlling. This means that the velocity of step 3 considerably exceeds the velocity of step 2 *reverse*. Under these conditions, the general rate expression 4 reduces to equation 5.[4]

$$k_{obsd} = \frac{[B]}{[B]_{stoich}} \Sigma k_{2i}[HA_i]f_B f_{HA_i}/f_{tr_{2i}} \quad (5)$$

The expression for the isotope effect for deuteroaldehyde in H_2SO_4 is equation 6, where B_D refers

$$k_{ArCHO}/k_{ArCDO} = \frac{[B]\ \Sigma k_{2i}[HA_i]f_B f_{HA_i}/f_{tr_{2i}}}{[B_D]\ \Sigma k^D_{2i}[HA_i]f_{B_D}f_{HA_i}/f^D_{tr_{2i}}} \quad (6)$$

to free deuteroaldehyde. Since the hydrogen and deuteroaldehydes have experimentally identical basicity, $[B]/[B_D] = 1$. Furthermore, it is reasonable to expect k_{2i} for each proton solvent acid species to be practically the same for the deuteroaldehyde as for the hydrogen aldehyde. Also, it is reasonable to expect $f_B/f_{tr_{2i}} = f_{B_D}/f^D_{tr_{2i}}$ for

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(8)(a) In this respect the behavior of 2,4,6-trialkylbenzaldehydes is like that of other typical oxygen bases, such as acetophenone. That is, in mineral acid media in which the conjugate acid ultraviolet peak is experimentally detectable, the peak is fully formed by the time the spectrum is measured, and probably in a much shorter time.

(8)(b) There is no exchange of aldehydic deuterium during decarbonylation as shown by the following experiments: 2,4,6-triisopropylbenzaldehyde-d_1 (300 mg.) was treated at 80° with 85% and 95% H_2SO_4, respectively (30 ml.), for a sufficient length of time to allow decarbonylation to proceed to from one to two half-lives; the aldehyde recovered from each reaction mixture had an infrared spectrum identical to starting aldehyde, including the prominent C–D stretching bands at 4.75 and 4.85 μ.

each i in all the sulfuric acid percentages. Therefore, for step 2 forward rate controlling, the expected $k_{\text{ArCHO}}/k_{\text{ArCDO}}$ ratio is unity, as observed.

With step 2 forward rate controlling the expression for the isotope effect in deuterated mineral acid *vs.* protonated mineral acid for hydrogen aldehyde is given by equation 7.

$$k_{\text{H}_2\text{SO}_4}/k_{\text{D}_2\text{SO}_4} = \frac{[\text{B}]_{\text{in H}_2\text{SO}_4}\ \Sigma k_{2\text{i}}[\text{HA}_\text{i}]f_\text{B}f_{\text{HAi}}/f_{\text{tr2i}}}{[\text{B}]_{\text{in D}_2\text{SO}_4}\ \Sigma k_{\text{D2i}}[\text{DA}_\text{i}]f_\text{B}f_{\text{DAi}}/f^{\text{D}}_{\text{tr2i}}} \quad (7)$$

There are two factors that would act to make $k_{\text{H}_2\text{SO}_4}/k_{\text{D}_2\text{SO}_4}$ greater than unity. Firstly, since $k_{2\text{i}}$ is a rate constant for proton transfer from a solvent acid species, it is reasonable to expect $k_{2\text{i}} > k_{\text{D}_2\text{i}}$ for each i. Secondly, since equilibrium 1 lies further to the right in D_2SO_4–D_2O than in H_2SO_4, the ratio [B] in H_2SO_4/[B] in D_2SO_4 is greater than unity; experimentally this ratio is equal to 2.0. Thus the *direct* isotope effect in the rate-controlling step, 2 forward, is half of the experimentally observed $k_{\text{H}_2\text{SO}_4}/k_{\text{D}_2\text{SO}_4}$ ratio. Unpredictable differences in $a_{\text{HA}_\text{i}}f_\text{B}/f_{\text{tr}_{2\text{i}}}$ *vs.* $a_{\text{DA}_\text{i}}f_\text{B}/f_{\text{tr}_{2\text{i}}}$, presumably small, also could modify the isotope effect.

It seems clear that the isotope effects in >85% mineral acid are completely consistent with step 2 forward rate controlling in these percentages. This is further confirmed by the observations that $k_{\text{ArCHO}}/k_{\text{ArCDO}}$ is unity in 90.9% D_2SO_4–D_2O (Table I), and that $k_{\text{H}_2\text{SO}_4}/k_{\text{D}_2\text{SO}_4}$ in 90.9% acid has the same value for ArCDO as for ArCHO (Table II).

The isotope effects in the lower mineral acid percentages, 70–85%, are consistent with step 2 *forward* being at least largely rate-controlling. However, the $k_{\text{ArCHO}}/k_{\text{ArCDO}}$ ratio, though near unity, is greater than unity by an amount significantly greater than the experimental error. Furthermore, there is a noticeable decline in the $k_{\text{H}_2\text{SO}_4}/k_{\text{D}_2\text{SO}_4}$ ratio that is not all attributable to the decline in the ratio $[\text{B}]_{\text{in H}_2\text{SO}_4}/[\text{B}]_{\text{in D}_2\text{SO}_4}$. This may indicate that in the lower acid percentages step 3 has entered to a slight extent as a rate-controlling step. If it is assumed that $k_{\text{ArCHO}}/k_{\text{ArCDO}}$ would be exactly unity if step 2 forward were completely rate-controlling and the isotope effect on the deuteroaldehyde in step 3 has the value of 3 (the maximum value in the step 3 isotope effect observed for mesitaldehyde was 2.8),[4] then about a 15% contribution of step 3 to the rate-controlling processes would be required to make $k_{\text{ArCHO}}/k_{\text{ArCDO}} = 1.25$. This amount of contribution of step 3 would also act to reduce the observed $k_{\text{H}_2\text{SO}_4}/k_{\text{D}_2\text{SO}_4}$ ratio by about 0.6.

2,4,6-Triisopropylbenzaldehyde *vs.* Mesitaldehyde.—For 2,4,6-triisopropylbenzaldehyde in >85% mineral acid the isotope effects indicate that step 2 forward is practically completely rate controlling; for mesitaldehyde in >85% acid, the isotope effects indicated that *both* step 2 forward and step 3 are rate-controlling steps of comparable magnitude.[4] This means that when the substrate is changed from mesitaldehyde to 2,4,6-triisopropylbenzaldehyde, there is a decrease in the velocity of step 2 *reverse relative to* step 3. Thus there has been a full realization of the expectation that this would occur, based on a predicted reduction in the relative catalytic effectiveness of bisulfate ion in step 2 *reverse*; *i.e.*, $k_{-2\text{HSO}_4^\ominus}/k_{-2\text{H}_2\text{O}}$ decreases in changing from mesitaldehyde to 2,4,6-triisopropylbenzaldehyde, and more so than does $k_{3\text{HSO}_4^\ominus}/k_{3\text{H}_2\text{O}}$.

For 2,4,6-triisopropylbenzaldehyde in the lower mineral acid percentages (<85%), the isotope effects indicate that step 2 forward is largely rate controlling; for mesitaldehyde in <85% mineral acid, the isotope effects indicate that step 3 is rate controlling.[4] This means that in these acid percentages as well there is a decrease in the velocity of step 2 *reverse relative to* step 3. Since water is no doubt the principal participating base in the less concentrated sulfuric acid solutions, it can be concluded that the catalytic effectiveness of water in step 2 *reverse relative to* 3 is reduced in changing from mesitaldehyde to 2,4,6-triisopropylbenzaldehyde (*i.e.*, $k_{-2\text{H}_2\text{O}}/k_{3\text{H}_2\text{O}}$ less for triisopropylbenzaldehyde). This conclusion is in agreement with the prediction that steric strain in the transition state would act to slow down step 2 *reverse* relative to step 3.

It should be pointed out that the ratio $v_{-2}/v_3 = \Sigma k_{-2\text{i}}a_{\text{Ai}}f_{\text{BH}^{*\oplus}}/f_{\text{tr}_{2\text{i}}}/\Sigma k_{3\text{i}}a_{\text{Ai}}f_{\text{BH}^{*\oplus}}/f_{\text{tr}_{3\text{i}}}$ may vary with mineral acid percentage (and aldehyde structure) for reasons other than $k_{-2\text{HSO}_4^\ominus}/k_{-2\text{H}_2\text{O}}$ less than $k_{3\text{HSO}_4^\ominus}/k_{3\text{H}_2\text{O}}$. Thus, even *if* the solvent basic species should have the same *relative* effectiveness in step 2 reverse as in step 3 (*i.e.*, $k_{-2\text{HSO}_4^\ominus}/k_{-2\text{H}_2\text{O}} = k_{3\text{HSO}_4^\ominus}/k_{3\text{H}_2\text{O}}$), changes in the ratio $f_{\text{tr}_{3\text{i}}}/f_{\text{tr}_{2\text{i}}}$ with acid percentage and with aldehyde structure would produce changes in v_{-2}/v_3. However, we believe it is highly unlikely that the activity coefficient ratio of such similarly constituted transition states would vary in the extreme fashion necessary to change the ratio v_{-2}/v_3 from a value considerably greater than unity to a value considerably less than unity.[9]

General Catalysis, Specific Oxonium Ion Catalysis and the Hammett Mechanism.—The Hammett "unimolecular" mechanism,[10] equations 8 and 9, is clearly excluded for the aromatic decarbonylation reaction by the experimental facts, including both the isotope effects for mesitaldehyde[4] and 2,4,6-triisopropylbenzaldehyde and the change in k_{obsd} over a wide range of sulfuric acid percentage for mesitaldehyde, 2,4,6-triethylbenzaldehyde and 2,4,6-triisopropylbenzaldehyde.[3] Nevertheless, k_{obsd} for mesitaldehyde in about 75–95% sulfuric acid, which represents a goodly portion of the total range of sulfuric acid in which the reaction was studied (59–100%), changes in a manner consistent with the Hammett mechanism[3]; *i.e.*, equation 10 or 11 is followed.[11] Since this mechanism cannot be

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(9) For a discussion of activity coefficient ratios in concentrated sulfuric acid see: N. C. Deno and R. W. Taft, Jr., THIS JOURNAL, **76**, 1 (1954), and N. C. Deno and C. Perizzolo, *ibid.*, **79**, 1345 (1957).

(10) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chapter IX.

(11) Equation 10 is the proper equation to use when the substrate base, B, is in equilibrium with appreciable amounts of other species.[12] When the only other substrate species present in appreciable amounts is the conjugate acid, $\text{BH}^\oplus$, equation 11 is equivalent to equation 10.[13] When the substrate is practically all in the form of the free base, then $[\text{B}] = [\text{B}]\text{stoich}$ and $K_\text{a}/h_0 \ll 1$, and both equations 10 and 11 reduce to the more familiar form, $\log k_{\text{obsd}} + H_0 = \text{const.}$ In the aldehyde decarbonylation the term $\log([\text{B}]/[\text{B}]_{\text{stoich}})$ makes an appreciable contribution; *i.e.*, equilibrium 1 lies to the right in the sulfuric acid media used. In fact, beyond 80% H_2SO_4 equilibrium 1 lies so far to the right that $[\text{B}] \ll [\text{BH}^\oplus] = [\text{B}]_{\text{stoich}}$ and hence $\log([\text{B}]/[\text{B}]_{\text{stoich}}) = H_0 - pK_\text{a}$. Thus, the prediction of equation 10 or 11 (of course, under the assumption that $f_{\text{BH}^\oplus}/f_{\text{tr}^\oplus}$ is constant)[10] is that $\log k_{\text{obsd}}$ should be constant beyond 80% H_2SO_4.

operative here, it had been concluded that agreement with the Hammett equation (*i.e.*, equation 10

$$B + H^{\oplus} \text{ (solvated proton)} \rightleftarrows BH^{\oplus} \quad (8)$$

$$BH^{\oplus} \longrightarrow [tr^{\oplus}] \longrightarrow \text{Prods} \quad (9)$$

$$\log k_{\text{obsd}} + H_0 - \log([B]/[B]_{\text{stoich}}) = \text{const.}$$
$$\text{assumes } f_{BH^{\oplus}}/f_{tr^{\oplus}} = \text{const.} \quad (10)$$

$$\log k_{\text{obsd}} - \log\left(h_0 \middle/ \left(1 + \frac{K_a}{h_0}\right)\right) = \text{const.}$$
$$\text{assumes } f_{BH^{\oplus}}/f_{tr^{\oplus}} = \text{const.} \quad (11)$$

or 11) over a limited range of mineral acid percentage is *not a sufficient* criterion for the assignment of mechanism.[14]

An attempt is here made to give a rational answer to the following questions: (1) What are the necessary conditions for the mechanism of successive bimolecular proton transfer steps (equations 1, 2 and 3) to give agreement with equation 10 or 11, derived for a "unimolecular" process? (2) Why does mesitaldehyde decarbonylation give reasonably good agreement with equation 10 or 11 over a considerable range of acid percentage? (3) Why is the deviation from "apparent" unimolecular behavior so much more marked for the decarbonylation of 2,4,6-triisopropylbenzaldehyde? For an answer to these questions, consider first the general rate expression, equation 4, for the mechanism of successive bimolecular proton transfer steps.[16] The quantity $[B]/[B]_{\text{stoich}}$ can be expressed in terms of h_0, as in equation 12.

$$[B]/[B]_{\text{stoich}} = [B]/([B] + [BH^{\oplus}]) = \frac{1}{1 + (K_a^{BH^{\oplus}}/h_0)} \quad (12)$$

where $K_a^{BH^{\oplus}} = a_{H^{\oplus}}a_B/a_{BH^{\oplus}}$ and $h_0 = a_{H^{\oplus}}f_B/f_{BH^{\oplus}}$. Then, if $v_3 >> v_{-2}$ (*i.e.*, step 2 rate-controlling), or alternatively, if v_{-2}/v_3 is constant with changing mineral acid percentage,[18] equation 4 can be converted to 13. Under the *further condition* that the acidic catalytic constants for step 2, k_{2i}, have the same ratio as for the indicator base, the quantity $\Sigma k_{2i}[HA_i]f_Bf_{HA_i}/f_{tr_{2i}}$ is equivalent to the quantity $k_2a_{H^{\oplus}}f_B/f_{tr^{\oplus}}$, where $a_{H^{\oplus}}$ has the connotation given it by Hammett.[10] Equation 13 would then reduce to 14. In *log* form equation 14 is iden-

$$k_{\text{obsd}} = \frac{\text{Const.}}{1 + (K_a^{BH^{\oplus}}/h_0)} \Sigma k_{2i}[HA_i]f_Bf_{HA_i}/f_{tr_{2i}} \quad (13)$$

$$k_{\text{obsd}} = \frac{\text{Const.}}{1 + (K_a^{BH^{\oplus}}/h_0)} a_{H^{\oplus}}f_B/f_{tr^{\oplus}} \quad (14)$$

tical to equation 11, derived for the "unimolecular" mechanism (equations 8 and 9). Thus if the conditions (1) either $v_3 >> v_{-2}$ or v_{-2}/v_3 constant, and (2) the catalytic constants for solvent acids, k_{2i}, have a "normal" catalytic ratio, are satisfied, then k_{obsd} would change in the same manner for the mechanism of successive bimolecular proton transfer steps as for the unimolecular mechanism. The "normal" catalytic constant ratio is defined as the catalytic constant ratio that prevails in the indicator acid–base equilibrium. When the "normal" catalytic constant ratio is sufficiently disturbed, in step 2, by substrate structural effects, then deviations from equation 11 or 10 should be discernible.

The above conditions are not met in the decarbonylation of mesitaldehyde, and deviations from equation 10 or 11 are found in the low and high sulfuric acid percentages (see Fig. 2). However, equation 10 or 11 is followed quite well in 75–95% H_2SO_4. In the first place, neither the condition $v_3 >> v_{-2}$ or v_{-2}/v_3 constant is satisfied. In the second place, the acid catalysis constants, k_{2i}, do not have the "normal" ratio. In particular, the catalytic effectiveness of H_2SO_4 relative to $H_3O^{\oplus}$ is reduced below the normal ratio. This follows from the conclusion, based on experiment, that in step 2 *reverse* the catalytic effectiveness as a base of bisulfate ion relative to H_2O has been reduced (previous section). That is to say, in step 2 *reverse*, the energy of the transition state with bisulfate ion as the base has been raised relative to the energy of the

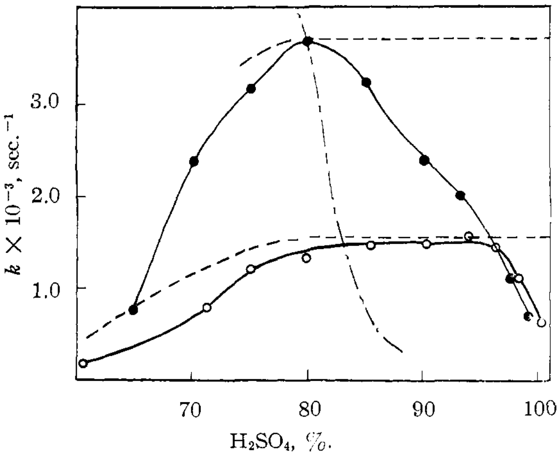

Fig. 2.—Plot of k *vs.* % H_2SO_4: ○, experimental points for mesitaldehyde; ●, experimental points for 2,4,6-triisopropylbenzaldehyde; – – –, calculated for both aldehydes from equation 10, assuming the Hammett mechanism; – – – – – –, calculated for 2,4,6-triisopropylbenzaldehyde from equation 16, assuming a specific oxonium ion catalysis. Calculated curves were anchored at the maxima of the observed curves.

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[12] W. M. Schubert and H. K. Latourette, THIS JOURNAL, **74**, 1829 (1952).

[13] M. Paul and F. A. Long, *Chem. Revs.*, **57**, 935 (1957).

[14] For most reactions to which the Hammett equation has been applied, the substrate has been largely in the form of the free base, *i.e.*, $[B] = [B]_{\text{stoich}}$ and equation 10, or 11, reduces to $\log k_{\text{obsd}} + H_0 = \text{const.}$ Because of this, the observed rate constant increased very rapidly with increasing mineral acid percentage. It was therefore experimentally practical to study these reactions only over a limited range of mineral acid percentage, generally less than 10%.[15]

[15] L. P. Hammett and A. J. Deyrup, THIS JOURNAL, **54**, 2721 (1932).

[16] Throughout this discussion it is presumed that the "solvated" proton, denoted by Hammett as $H^{\oplus}$,[10] actually exists in more than one potential energy well; hence the use of the symbols HAi and Ai. For example, in strong sulfuric acid, the proton is presumed to exist in mainly two potential wells. That is to say, some of the protons are primarily bonded to water (*i.e.*, covalently bonded) and secondarily to other basic species (*i.e.*, by hydrogen-bonding); others are primarily bonded to bisulfate ion. For protons in the former potential well the symbol $H_3O^{\oplus}$ is used; for protons in the latter potential well, the symbol H_2SO_4 is used. In this connection, Falk and Giguère have very recently obtained infrared spectral evidence for the distinct existence of the species $H_3O^{\oplus}$ in strong acid solutions.[17] We believe that the term "solvated proton" may be unfortunate, insofar as it may give the impression that the proton exists in but a single potential energy well.

[17] M. Falk and P. A. Giguère, *Chem. Eng. News*, **35**, 59 (1957).

[18] This requires $k_{-2H_2SO_4^{\ominus}}/k_{-2H_2O} = k_{3HSO_4^{\ominus}}/k_{3H_2O}$. Such a condition is probably not generally met; see references 5 and 6.

transition state with H_2O as the base. Since step 2 *forward* proceeds through the same transition states, it follows that the catalytic constant for H_2SO_4, $k_{2H_2SO_4}$, is suppressed somewhat *relative to* the catalytic constant for $H_3O^{\oplus}$, $k_{2H_3O^{\oplus}}$. This means that the quantity $\Sigma k_{2i}[HA_i]f_Bf_{HA_i}/f_{tr_{2i}}$ of equation 4 would *increase* with percentage sulfuric acid to a somewhat *lesser* extent than does h_0. However, the numerator of equation 4 is at the same time *decreasing* slowly with an increase in percentage sulfuric acid, since the ratio v_{-2}/v_3 (which is comparable in value to unity in >85% acid) is decreasing. Thus there will be a region of sulfuric acid in which the entire quantity $\Sigma k_{2i}[HA_i]f_Bf_{HA_i}/f_{tr_{2i}}/(1 + v_{-2}/v_3)$ could change approximately with h_0, resulting in good agreement with equation 11 (as observed in 75–95% H_2SO_4). This entire quantity would then show less of an increase with percentage H_2SO_4 than does h_0 when v_{-2}/v_3 begins to get small relative to unity (*i.e.*, in the highest H_2SO_4 percentages, in which step 2 forward is fighting for full rate-control). Since the quantity $[B]/[B]_{stoich}$ of equation 4 is *decreasing* in proportion to h_0 in this region, the net result should be a decline in k_{obsd} and a deviation from equation 11 (see Fig. 2).

In the decarbonylation of triisopropylbenzaldehyde, the quantity $\Sigma k_{2i}[HA_i]f_Bf_{HA_i}/f_{tr_{2i}}$ should be increasing even less rapidly with increasing percentage H_2SO_4 than in the decarbonylation of mesitaldehyde. This would be true because the catalytic effectiveness of H_2SO_4 relative to $H_3O^{\oplus}$ in step 2 forward is reduced even further. Furthermore, the denominator of equation 4 is not suffering any compensating decrease with increasing acid percentage. This is because v_{-2}/v_3 remains small relative to 1; *i.e.*, step 2 forward is completely rate-controlling in the high acid percentages and at least largely so in the lower acid percentages (previous section). As a result, deviations from equation 11 are very large and the decline in k_{obsd} in the higher H_2SO_4 percentages begins sooner and is much more rapid than for mesitaldehyde.

The greater decline in the catalytic effectiveness of H_2SO_4 relative to $H_3O^{\oplus}$ in step 2 means that triisopropylbenzaldehyde decarbonylation lies nearer (though not necessarily close to) the extreme of experimental specific oxonium ion catalysis than does mesitaldehyde decarbonylation. A test can be made of whether or not triisopropylbenzaldehyde decarbonylation lies at the extreme of specific oxonium ion catalysis. Equation 5, the rate equation that applies when step 2 forward is rate-controlling, reduces to equation 15 in the event of negligible catalysis by H_2SO_4

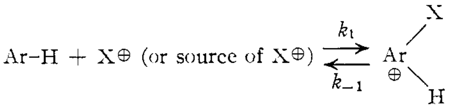
$$k_{obsd} = \frac{[B]}{[B]_{st.}} k_2 a_{H_3O^{\oplus}} f_B/f_{tr_2^{\oplus}} \qquad (15)$$

Since $a_B a_{H_3O^{\oplus}} = K a_{H_2O} a_{BH^{\oplus}}$, equation 15 is equivalent to 16.

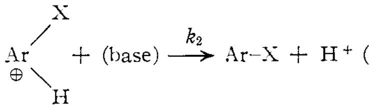
$$k_{obsd} = \frac{[BH^{\oplus}]}{[B]_{stoich}} K k_2 a_{H_2O} f_{BH^{\ominus}}/f_{tr_2^{\oplus}} \qquad (16)$$

Equation 16 is plotted for 2,4,6-triisopropylbenzaldehyde in Fig. 2; the usual assumption that $f_{BH^{\oplus}}/f_{tr^{\oplus}}$ is constant[10] has been made in constructing this plot. From a comparison of the experimental change in k_{obsd} with percentage H_2SO_4 with the change calculated from equation 16, it is clear that the decarbonylation of triisopropylbenzaldehyde does not follow specific oxonium ion catalysis. Also shown in Fig. 2 is a plot of k_{obsd} against const. $[B]h_0/[B]_{stoich}$ in order that the deviation from "Hammett-like" behavior may also be seen. It can be concluded that the triisopropylbenzaldehyde decarbonylation involves a general acid catalysis that lies between "normal" general acid catalysis and the extreme of specific oxonium ion catalysis. By the same token, the decarbonylation of mesitaldehyde lies closer to "normal" general acid catalysis.

The Mechanism of Aromatic Electrophilic Substitution.—The aromatic decarbonylation reaction is an example of aromatic electrophilic substitution; it differs from the more common types in that the electrophilic species is a proton (strictly speaking, a proton source) and the group being displaced is not. The present study has a bearing on the question of whether aromatic electrophilic substitution in general is a two-step process proceeding *via* an intermediate (represented approximately by equations 17 and 18) or a one-step process (equation 19).[19–26]

 (17)

$$\text{Ar–H} + X^{\oplus}\text{ (or source of }X^{\oplus}) \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \overset{\oplus}{\text{Ar}}(X)(H) \qquad (17)$$

 (18)

$$\overset{\oplus}{\text{Ar}}(X)(H) + \text{(base)} \xrightarrow{k_2} \text{Ar–X} + H^{+}\text{ (bound to base)} \qquad (18)$$

$$\text{Ar–H} + X^{\oplus} \longrightarrow \text{transition state} \longrightarrow \text{ArX} + H^{\oplus} \qquad (19)$$

Efforts to determine whether the substitution occurs *via* an intermediate have involved the use of deuterated or tritiated aromatic compounds. In some instances no isotope effect was found when rates of normal and labeled compounds were compared; these include the nitration of benzene,[21] toluene,[19] bromobenzene,[19] naphthalene[19] and nitrobenzene,[20,21] and the bromination of benzene[19,22] and bromobenzene.[22] These results are consistent with the mechanism of equations 17 and 18 with step 1 forward rate-controlling (*i.e.*, $v_{-1} << v_2$). However, as pointed out by Hammond,[26] such results *taken alone* do not rigorously exclude the one-step mechanism, equation 19.[27] In several other aromatic electrophilic substitution reactions, isotope effects have been observed. Examples include sulfonation of bromobenzene (k_H/k_T = 1.8),[19] cyclodehydration of 2-anilino-pent-2-ene-4-

[19] L. Melander, *Arkiv Kemi*, **2**, 211 (1950); **6**, 219 (1953); *Acta Chim. Scand.*, **3**, 95 (1949).

[20] T. G. Bonner, F. Bowyer and G. Williams, *J. Chem. Soc.*, 2650 (1953).

[21] W. M. Lauer and W. E. Noland, THIS JOURNAL, **75**, 3689 (1953).

[22] P. D. B. de la Mere, T. M. Dunn and J. T. Harvey, *J. Chem. Soc.*, 923 (1957).

[23] H. Zollinger, *Helv. Chim. Acta*, **38**, 1597, 1617, 1623 (1955).

[24] T. G. Bonner and J. M. Wilkins, *J. Chem. Soc.*, 2358 (1955).

[25] E. Grovenstein, THIS JOURNAL, **79**, 2972 (1957).

[26] G. S. Hammond, *ibid.*, **77**, 334 (1955).

[27] More precisely, one can conclude from this evidence alone that stretching of the C–H bond has not made much progress in the transition state of the slow step(s) of the reaction (see ref. 26).

one (k_H/k_D = 1.5)[20] and the iodination of phenol (k_H/k_D = 4).[25] These results are consistent with the two-step mechanism, with step 2 at least partially rate-controlling (*i.e.*, v_{-1} comparable to or greater than v_2). Alternatively, these results can be accommodated by the one-step mechanism, 19, with C–H bond stretching having made measurable progress in the transition state. However, the two-step mechanism more reasonably accounts for both types of observations, *i.e.*, examples in which no isotope effect was found and those in which there was an isotope effect.

Perhaps the best evidence in favor of the two-step mechanism is the excellent work of Zollinger.[23] It was found that the rate of diazonium salt coupling with the unhindered 1-naphthol-4-sulfonic acid was essentially the same for the 2-deutero as for the unlabeled compound. However, the isotope effect for the coupling of the hindered 1-deutero-2-naphthol-6,8-disulfonic acid with various diazonium salts was considerable. The k_H/k_D ratio varied from 4.8 to 6.5, depending on the structure of the diazonium salt. The results were interpreted in terms of the two-step mechanism, with varying contributions of the second step to the rate-controlling processes. Base catalysis (by amines) was observed for the hindered naphthol but not for the unhindered naphthol. In addition, the catalytic effect of the base decreased as its size was increased. Zollinger's results are completely consistent with the two-step mechanism and would be difficult indeed to rationalize in terms of the one-step mechanism.

The aromatic decarbonylation is in many respects quite similar to the reaction studied by Zollinger. That is, the experimental findings show that the substitution proceeds *via* an intermediate (specifically $BH^{\oplus *}$, equation 2). Also, by a suitable change in the medium and in substrate structure, the rate-controlling step can be changed from one in which the intermediate is formed to one in which it is decomposed. Moreover, the situation has been achieved in which these two steps are *both* rate-controlling steps of comparable magnitude.

The two-step mechanism then rationally accounts for all the results cited in this section, taken separately and as a whole. The one-step mechanism can be fitted only to some of the facts. It therefore is likely that most aromatic electrophilic substitution reactions, if not all, proceed *via* an intermediate.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

Ionic Polymerization. Reactions of α-Ethylstyrene and *cis*- and *trans*-α,β-Dimethylstyrene with Stannic Chloride[1]

BY C. G. OVERBERGER, ELI M. PEARCE[2] AND D. TANNER[2]

RECEIVED OCTOBER 24, 1957

Reaction of α-ethylstyrene with stannic chloride at 0° for 1 hour gives a mixture of dimer (78%) and trimers (16%). The dimer was characterized as 3,5-diphenyl-5-methyl-2-heptene. After 24-hour contact with catalyst the cyclic dimer, 1,3-diethyl-1-methyl-3-phenylhydrindane, (46%) was isolated. A suggestion is made for the lack of polymer formation on the basis of steric factors. *cis*-α,β-Dimethylstyrene, after contact with stannic chloride for 24 hours, gave a mixture of dimers (31%) from which 3,5-diphenyl-5-methyl-2-heptene was characterized. *trans*-α,β-Dimethylstyrene did not react under these conditions.

α-Methylstyrene homopolymerized very rapidly with cationic catalysts[3] and has been copolymerized with a variety of substituted styrenes,[4] including *p*-chlorostyrene.[5] Values obtained for the monomer reactivity ratios for the system α-methylstyrene, *p*-chlorostyrene and stannic chloride as catalyst were indicative of the enhanced reactivity of α-methylstyrene under these conditions, which can be understood on the basis of polar and resonance effects. The electron-donating effect of the methyl group attached directly to the double bond increases the reactivity of the monomer toward a carbonium ion. In addition, the carbonium ion formed from α-methylstyrene has increased resonance stabilization due to hyperconjugation effects when compared with styrene.

When the methyl group in the α-position was lengthened by a methylene unit the following anomalous observations were made: (a) homopolymerization with stannic chloride as catalyst did not occur; (b) copolymerization with *p*-chlorostyrene gave different copolymer composition curves with scattering considerably beyond experimental error. From these data, it would seem that the reactivity of α-ethylstyrene was much less than that of *p*-chlorostyrene, a somewhat unexpected result not easily explained by steric factors alone. The present research was initiated to explain the above phenomena.

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[1] This is the 8th in a series of papers in the general field of ionic-catalyzed polymerization. For the previous paper in this series, see C. G. Overberger, G. F. Endres and Avito Monaci, THIS JOURNAL, **78**, 1969 (1956).

[2] This paper comprises portions of theses presented by D. Tanner and Eli M. Pearce in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the Polytechnic Institute of Brooklyn.

[3] A. B. Hersberger, J. C. Reid and R. G. Heiligmann, *Ind. Eng. Chem.*, **37**, 1073 (1945); D. C. Pepper, *Trans. Faraday Soc.*, **45**, 397 (1949).

[4] C. G. Overberger, *et al.*, THIS JOURNAL, **74**, 4848 (1952).

[5] (a) G. Smets and L. deHaes, *Bull. soc. chim. Belges*, **59**, 13 (1950); (b) C. G. Overberger, L. H. Arond and J. J. Taylor, THIS JOURNAL, **73**, 5541 (1951).