press their appreciation for the suggestions made by Professors G. E. Kimball and W. E. Doering, and Dr. J. Q. Umberger.

WILMINGTON, DELAWARE RECEIVED APRIL 20, 1950

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DIVISION, POLYMER CORPORATION LIMITED]

The Cumene Hydroperoxide–Iron(II) Reaction in the Absence of Oxygen[1]

BY J. W. L. FORDHAM AND H. LEVERNE WILLIAMS

In dilute aqueous solutions of low *p*H and in the absence of monomer the ratio of iron(II) oxidized to cumene hydroperoxide consumed is less than one to one. In the presence of acrylonitrile experimental data indicate that iron(II) disappears only by the bimolecular reaction involving iron(II) and cumene hydroperoxide. In the temperature range from 0 to 25° the rate constant of this primary reaction is given by $k_1 = 1.07 \times 10^{10}\, e^{-12{,}000/RT}$ l. mole^{-1} sec.$^{-1}$. The amount of reaction between the hydroperoxide and the tri-α,α'-bipyridyl complex of iron(II) is negligible initially at least. The presence of dihydroxyacetone results in a slight lowering of the ratio of iron(II) oxidized to hydroperoxide consumed. In 0.1 *N* NaOH there is a rapid reaction between the hydroperoxide and the monomer, acrylonitrile.

Introduction

This paper is the fourth of a series[2,3,4] on a study of cumene hydroperoxide (CHP) as a polymerization initiator. In the third paper it was reported that the rate constant (k_1) of the primary radical producing reaction in the temperature range from 0 to 25° is given by $k_1 = 3.9 \times 10^9\, e^{-11{,}100/RT}$ l. mole^{-1} sec.$^{-1}$. In those experiments an excess of oxygen was present, and to simplify the algebraic equations two assumptions were made. The first assumption was that the contribution to the total rate of disappearance of iron(II) made by the reactions between iron(II) and the hydroperoxides formed during the reaction is negligible during the initial stages because of the low concentrations of those hydroperoxides initially. The other assumption was that the primary rate constant is considerably smaller than those of certain subsequent reactions. However the slight dependence of the rate constant on the initial concentrations of CHP and iron(II) indicated that any value obtained from experiments conducted in an oxygen atmosphere might be too large. Furthermore there was the added inducement of measuring the rate constant in the presence of a monomer and in a nitrogen atmosphere. This report contains that work together with an account of the effect on the reaction of α,α'-bipyridyl and dihydroxyacetone (DHA), representative of two types of compounds used in low temperature polymerization recipes.

Theoretical

If the RO· radical, formed by the primary reaction

$$\mathrm{Fe^{++} + RO_2H \xrightarrow[k_1]{} Fe^{+++} + OH^- + RO\cdot}$$

where R represents the cumyl radical, $C_6H_5C(CH_3)_2$, reacts solely with a monomer molecule to initiate polymerization, the iron(II) should disappear by a second order reaction. Then eq. 1 should be valid.

$$\ln\,(1 + (a - b)/[\mathrm{Fe^{++}}]) = (a - b)k_1t + \ln a/b \quad (1)$$

where $a = [\mathrm{RO_2H}]_0$, initial CHP concentration and $b = [\mathrm{Fe^{++}}]_0$, initial iron(II) ion concentration. When $a < b$ and $t \rightarrow \infty$

$$(b - a) = [\mathrm{Fe^{++}}]_\infty \quad (2)$$

where $[\mathrm{Fe^{++}}]_\infty = [\mathrm{Fe^{++}}]$ at infinite time. Equation 2 was used to determine $(b - a)$ rather than the difference between the initial concentration of iron(II) and hydroperoxide because an initial reaction involving traces of oxygen, very difficult to remove experimentally, results in a decrease in the value of $(b - a)$ for the subsequent oxygen-free reaction.

When the complexing agent α,α'-bipyridyl (bip) is added to the system, the following equilibria are assumed to be valid.

$$\mathrm{Fe^{++} + bip \rightleftarrows Fe(bip)^{++}} \qquad K_1$$
$$\mathrm{Fe(bip)^{++} + bip \rightleftarrows Fe(bip)_2^{++}} \qquad K_2$$
$$\mathrm{Fe(bip)_2^{++} + bip \rightleftarrows Fe(bip)_3^{++}} \qquad K_3$$
$$\mathrm{(bip)H^+ \rightleftarrows bip + H^+} \qquad K_a$$

From these equilibria it can be derived that

$$[\mathrm{Fe(bip)^{++}}]/[\mathrm{Fe^{++}}] = K_1[\mathrm{bip}] = K_1([\mathrm{bip}]_T - [\mathrm{bip}]_c)\frac{K_a}{K_a + [\mathrm{H^+}]} \quad (3)$$

where $[\mathrm{bip}]_T$ = total bipyridyl concn. and $[\mathrm{bip}]_c$ = combined bipyridyl concn. If the ratio of $[\mathrm{Fe(bip)_2^{++}}]/[\mathrm{Fe^{++}}]$ is negligible compared to the ratio $[\mathrm{Fe(bip)^{++}}]/[\mathrm{Fe^{++}}]$

$$[\mathrm{Fe^{++}}] + [\mathrm{Fe(bip)^{++}}] = [\mathrm{Fe^{++}}]_T - [\mathrm{Fe(bip)_3^{++}}] \quad (4)$$

where $[\mathrm{Fe^{++}}]_T$ = total iron(II) concn. Equation 3 may be solved by trial and error substitution, and from eqs. 3 and 4 the concentration of uncomplexed iron(II), $[\mathrm{Fe^{++}}]$, may be determined.

Results

In 0.1 *N* sulfuric acid with $a = 4 \times 10^{-5}$ *M* and $b = 10 \times 10^{-5}$ *M* the stoichiometric ratio of iron(II) oxidized to CHP consumed in the absence of monomer at 25° was 0.85 to 1. Under these conditions the iron(II) does not disappear by a second order reaction. Under similar conditions in 0.1 *N* NaOH the ratio was 1.90 to 1, and the rate was much too rapid to measure even at this low concentration.

When acrylonitrile (AcN) is present under similar conditions in the acidic medium, the experimental

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[1] Presented before the Division of Inorganic and Physical Chemistry, American Chemical Society, Chicago, September, 1950.

[2] J. W. L. Fordham and H. L. Williams, *Can. J. Research*, **B27**, 943 (1949).

[3] J. W. L. Fordham and H. L. Williams, *ibid.*, **B28**, 551 (1950).

[4] J. W. L. Fordham and H. L. Williams, THIS JOURNAL, **72**, 4465 (1950).

data indicate that the iron(II) disappears by a second order reaction. The results are shown graphically in Figs. 1 to 3, and the values of the primary rate constants are presented in Table I.

TABLE I

PRIMARY RATE CONSTANTS FOR THE CHP–Fe^{++} REACTION

Temp., °C.	a $M \times 10^5$	b $M \times 10^5$	$[Fe^{++}]_\infty$ $M \times 10^5$	k_1 l. mole^{-1} sec.$^{-1}$
0.00	2.00	6.00	3.75	2.72
.00	4.00	6.00	1.70	2.70
.00	4.00	10.00	5.60	2.66
.00	8.00	10.00	1.06	2.64
.00	8.00	10.00	1.20	2.56[a]
.00	8.00	10.00	1.55	2.58[b]
12.50	2.00	6.00	3.90	6.85
12.50	4.00	6.00	1.90	7.00
12.50	4.00	10.00	5.50	7.05
12.50	8.00	10.00	1.55	6.95
25.10	2.00	6.00	3.90	17.6
25.10	4.00	6.00	1.75	16.2
25.10	4.00	10.00	5.70	16.8
25.10	8.00	10.00	1.85	17.6
25.10	8.00	10.00	2.57	17.7[c]

[a] [AcN] = 10^{-2} M instead of 10^{-1} M at zero time. [b] No H_2SO_4, final pH 3.5. [c] $[H^+] = 2 \times 10^{-2}$ M instead of 10×10^{-2} M, and 10×10^{-4} M DHA added.

In 0.1 N NaOH at room temperature the CHP reacted rapidly with AcN, and hence the rate of disappearance of iron(II) could not be followed in this system. The destruction of the hydroperoxide was verified experimentally by mixing an excess of AcN with CHP in 0.1 N NaOH, acidifying the solution in a few minutes, and noticing no disappearance of added iron(II) in the presence of oxygen.

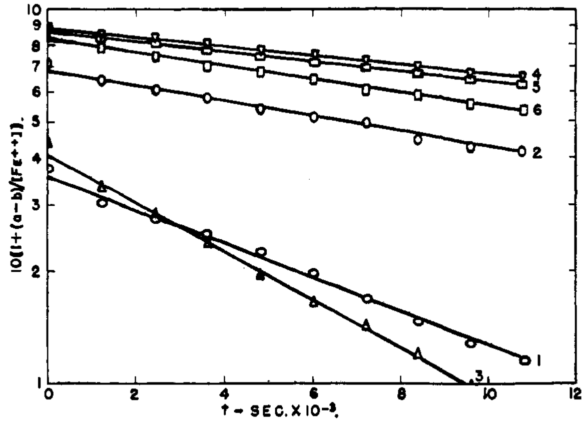

Fig. 1.—Reaction of cumene hydroperoxide and ferrous sulfate at 0°: curve 1, 2×10^{-5} molar CHP and 6×10^{-5} molar ferrous sulfate; curve 2, 4 and 6×10^{-5} molar, resp.; curve 3, 4 and 10×10^{-5} molar, resp.; curve 4, 8 and 10×10^{-5} molar, resp.; curve 5, same with 10^{-2} molar acrylonitrile; curve 6, same, no acid added.

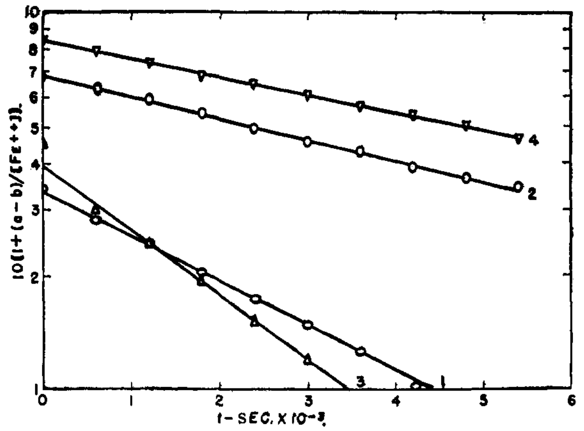

Fig. 2.—Reaction between cumene hydroperoxide and ferrous sulfate at 12.5°: curve 1, 2×10^{-5} molar CHP and 6×10^{-5} molar ferrous sulfate; curve 2, 4 and 6×10^{-5} molar, resp.; curve 3, 4 and 10×10^{-5} molar, resp.; curve 4, 8 and 10×10^{-5} molar, resp.

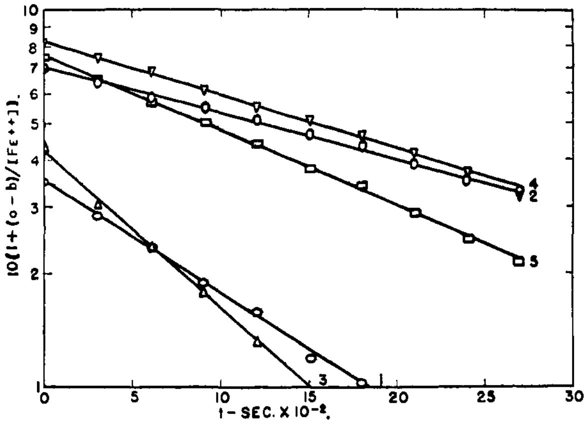

Fig. 3.—Reaction between cumene hydroperoxide and ferrous sulfate at 25.10°: curve 1, 2×10^{-5} molar CHP and 6×10^{-5} molar ferrous sulfate; curve 2, 4 and 6×10^{-5} molar, resp.; curve 3, 4 and 10×10^{-5} molar, resp.; curve 4, 8 and 10×10^{-5} molar, resp.; curve 5, 8 and 10×10^{-5} molar, resp. with 10×10^{-4} molar dihydroxyacetone and 2×10^{-2} N H_2SO_4.

The effect of an iron(II) complexing agent on the reaction was also studied using α,α'-bipyridyl as the complexing agent. α,α'-Bipyridyl was chosen because of its water solubility, its lack of interference with the bipyridyl method of analysis for residual iron(II), and the availability of quantitative information on the iron(II)–bipyridyl system.[5] Under the experimental conditions chosen the ratio $[Fe(bip)_2^{++}]/[Fe^{++}]$ was probably negligible compared to the ratio $[Fe(bip)^{++}]/[Fe^{++}]$, and the concentration of uncomplexed ferrous iron was determined by the method outlined previously. A comparison $(k_1)(a)(b)$ with the initial rate of total iron(II) disappearance determined from the plots in Fig. 4 is presented in Table II. Only initial values were checked because the presence of iron(III) formed during the reaction complicates the determination of uncomplexed iron(II) since iron(III) is also complexed by bipyridyl.

When 10×10^{-4} M DHA was added under conditions otherwise similar to the third experiment in Table II, the concentration of total iron(II) at corresponding times checked within $\pm 0.03 \times 10^{-5}$ M during the first 45 minutes of the reaction. Evidently no special effects are produced by the combination of bipyridyl with DHA.

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(5) J. H. Baxendale and P. George, *Trans. Faraday Soc.*, **46**, 55 (1950).

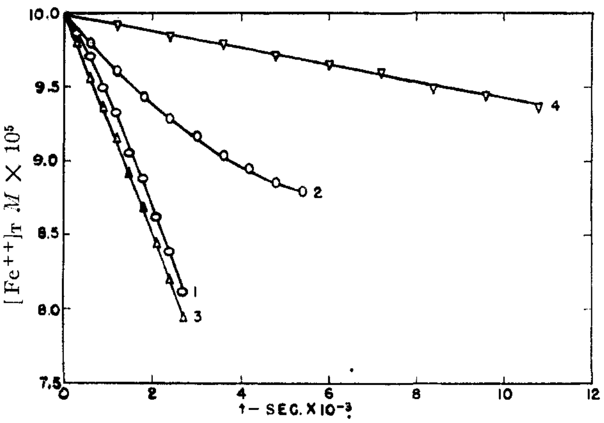

Fig. 4.—Reaction between cumene hydroperoxide (8 × 10^{-5} molar) and ferrous sulfate (10 × 10^{-5} molar) in the presence of 0.1 molar acrylonitrile at 25.10°: curve 1, 4.10 × 10^{-4} molar bipyridyl at *p*H 3.19; curve 2, 3.30 × 10^{-4} molar bipyridyl at *p*H 4.18; curve 3, 10.00 × 10^{-4} molar bipyridyl at *p*H 2.21; curve 4, same at *p*H 3.22.

TABLE II

COMPARISON OF INITIAL RATES OF DISAPPEARANCE OF Fe_T^{++}

$[bip]_T$ $M \times 10^4$	*p*H	$(k_1)(a)(b)$ mole sec.$^{-1}$ × 10^9	$-d[Fe^{++}]_T/dt^a$ mole sec.$^{-1}$ × 10^9
4.10	3.19	4.2	5.0
3.30	4.18	2.5	3.2
10.00	2.21	6.3	7.2
10.00	3.22	0.3	0.6

^{a} Indicates zero time. *b* is $[Fe^{++}]$ not total iron(II) concn. at zero time.

Discussion

The low stoichiometric ratio of iron(II) oxidized to CHP consumed in the acidic medium and in the absence of monomer may be explained by the radical induced decomposition of the CHP when no monomer or oxygen are present to react with the radical. However regeneration of iron(II) may be an alternative explanation. In the alkaline medium the reaction may proceed by an ionic mechanism.[6]

The relative constancy of the values of k_1 at each temperature in Table I indicates that a change in the initial concentrations of CHP, iron(II), AcN or hydrogen ion has no significant effect on the value of the rate constant within the limits tested at least. From these values the equation of this rate constant in the temperature range from 0 to 25° was determined to be $k_1 = 1.07 \times 10^{10} e^{-12,000/RT}$ l. mole^{-1} sec.$^{-1}$. A comparison of this equation with that obtained previously confirms the suspicion that the values obtained previously[4] were too large. It would seem that the reactions between iron(II) and the hydroperoxides formed in the presence of excess oxygen are not negligible even during the initial stages of the reaction.

From the values of $[Fe^{++}]_\infty$ in Table I it is obvious that traces of oxygen were present in the system and resulted in a stoichiometric ratio that was slightly greater than one to one. However, in view of the lack of significant change in the rate constant as the very small quantity of oxygen varied, it was concluded that the effect of traces of oxygen on the values of k_1 would be very small at the most. A much more elaborate apparatus would be necessary to study the reaction in the absence of still less oxygen.

The substitution of the cumyl group C_6H_5-$C(CH_3)_2$ for one hydrogen atom of hydrogen peroxide increases both the frequency factor (1.78 × 10^9 to 1.07 × 10^{10}) and the activation energy (10.1 to 12.0 kcal. per mole) of the primary rate constant so that from 0 to 25° the rate constant is approximately one quarter of that when hydrogen peroxide reacts with iron (II).[7]

In Table I it is also apparent that the presence of DHA may cause an increase in the apparent value of k_1 and a decrease in the stoichiometric ratio (0.93 to 1). Both these discrepancies may be explained by assuming that DHA radicals induce the decomposition of CHP or regenerate iron(II) from the iron(III) formed during the course of the reaction causing an increase in the apparent value of $(a - b)$. Kharasch[8] suggests that the latter reaction occurs with dextrose which acts similarly to dihydroxyacetone in polymerization reactions.[9]

The comparison of the rates in Table II indicates that under the experimental conditions tested the initial concentration of uncomplexed iron(II) is almost sufficient to account for the initial rate of disappearance of total iron(II). Furthermore if the assumption is made that the rate constant for the reaction between CHP and all the iron(II) with the exception of the tribipyridyl complex is approximately equal to k_1 then the initial concentration of this iron is slightly more than sufficient to account for all the initial rate of disappearance of total iron(II). Consequently the amount of reaction between CHP and $Fe(bip)_3^{++}$ would seem to be negligible initially at least, and in view of the relatively large concentration of the latter the rate constant of the CHP-tribipyridyl complex must be very small.

Experimental

The source and purity of the materials in addition to those described in the previous report[4] is: α,α'-bipyridyl, G. Frederick Smith Chemical Co., reagent grade; dihydroxyacetone, British Drug Houses, laboratory chemical; NaOH, Mallinckrodt Chemical Works, analytical reagent; acetate buffer (NaOAc, British Drug Houses, laboratory chemical; HOAc, Nichols Chemical Co., glacial acid); acrylonitrile, American Cyanamid Co., technical

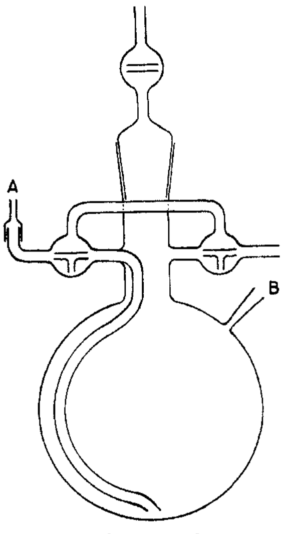

Fig. 5.—Diagram of apparatus.

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[6] C. E. Frank, *Chem. Revs.*, **46**, 155 (1949).

[7] J. H. Baxendale, M. G. Evans and G. S. Park, *Trans. Faraday Soc.*, **42**, 155 (1946).

[8] M. S. Kharasch, A. Fono and W. Nudenberg, *J. Org. Chem.*, **15**, 763 (1950).

[9] J. M. Mitchell, R. Spolsky and H. L. Williams, *Ind. Eng. Chem.*, **41**, 1592 (1949).

grade distilled under vacuum; nitrogen, Canadian Liquid Air Co. "oxygen-free" nitrogen bubbled twice through alkaline pyrogallol and then passed hot copper filings to remove traces of oxygen.

The reaction flask is illustrated in Fig. 5. By proper manipulation of the stopcocks nitrogen could be bubbled through the solution to displace oxygen and to stir the contents or nitrogen pressure could be used to force the solution into the sampling pipet inserted at A and then blow out the unused portion of the sample. After nitrogen had been bubbled through the solution for three-quarters of an hour, the deoxygenated final solution (iron(II) plus α,α'-bipyridyl, if used) was forced by nitrogen pressure into the flask through a buret inserted at B. Previous work showed that the order of addition of CHP and iron(II) was without effect at these low concentrations in the absence of monomer,[4] and the order probably would have still less effect when there is monomer present to react with the radicals which might induce hydroperoxide decomposition.

Samples were removed at intervals, centrifuged to remove any polyacrylonitrile if monomer were present initially and analyzed for residual iron(II) by the method outlined previously[4] along with the method of analysis for the CHP. The final iron(II) concentration was determined after a 24-hour period.

In the work on the effect of α,α'-bipyridyl on the reaction, the concentration of Fe(bip)$_3^{++}$ was measured colorimetrically with all reagents added except the CHP. In this determination it was assumed that absorption by the other complexes is negligible. Experimental evidence indicates that this is a valid assumption for the green filter (Klett-Summerson 54) used in these experiments since the optical density of a 1.0 × 10^{-1} *M* solution of iron(II) is unchanged on the addition of 3.0 × 10^{-5} *M* bipyridyl. Presumably this solution contains the Fe(bip)$^{++}$ and Fe(bip)$_2^{++}$ intermediates.[5] Acetate buffers were used to maintain *p*H values of 3 or 4. Lower *p*H values were obtained using sulfuric acid.

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SARNIA, ONTARIO, CANADA RECEIVED SEPTEMBER 25, 1950

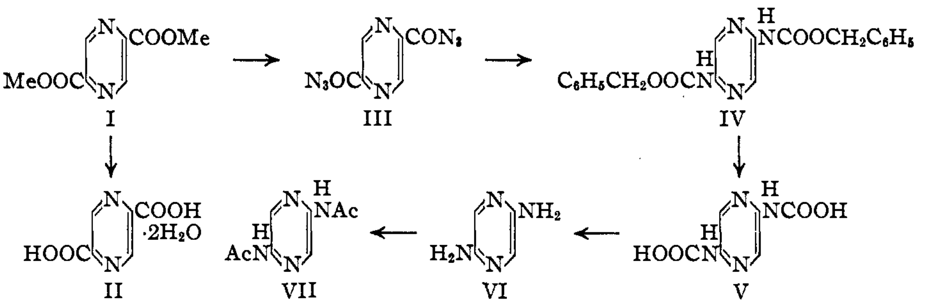
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

Syntheses in the Pyrazine Series; Synthesis of 2,5-Diaminopyrazine[1]

BY DAVID M. SHAREFKIN AND PAUL E. SPOERRI

The synthesis of 2,5-diaminopyrazine from its dibenzylurethan derivative is described. The failure of 2,5-dicarbomethoxypyrazine to undergo the Schmidt reaction is accounted for in terms of its normal ionization and "*i*" values in 100% sulfuric acid. 2,5-Dicarboxypyrazine dihydrate is obtained as the product of the Schmidt reaction. Also included are ultraviolet absorption spectra curves for 2,5-disubstituted pyrazines.

The preparation of 2,5-diaminopyrazine (VI) has been investigated in view of the recorded failure of others[2] to prepare this compound. During this investigation, the isomeric 2,3-diaminopyrazine was prepared by a Hofmann degradation[3] and the 2,6-diaminopyrazine by ammoniation[4] of the halogenated pyrazine. These reactions have failed to produce 2,5-diaminopyrazine.



Newman[5] and Smith[6] have pointed out that the Schmidt reaction should be acid catalyzed, preferably by the use of trichloroacetic acid in the sulfuric acid medium. The solid obtained from the acid-catalyzed Schmidt reaction on 2,5-dicarbomethoxypyrazine proved to be 2,5-dicarboxypyrazine dihydrate (II). The identity of the 2,5-dicarboxypyrazine dihydrate was established by analysis, and by electrometric titration with standard alkali. The curves obtained, by plotting *p*H *versus* alkali added, corresponded to the second stoichiometrical point, *i.e.*, for a weak dibasic acid.

To determine the extent of the preferential acid–base reaction between the pyrazine ring nitrogens and the solvent protons, that part of the Schmidt reaction mixture concerned with the formation of a pyrazine oxocarbonium ion was studied. The hydrolysis method of Hammett and co-workers[7] was used to determine the mode of ionization of 2,5-dicarbomethoxypyrazine in sulfuric acid solution. A solution of 2,5-dicarbomethoxypyrazine (I) in cold concentrated sulfuric acid was poured into ice water. The ester was recovered unchanged, indicating its normal ionization in the medium.

Quantitative determination of "*I*" values for 100% sulfuric acid solutions of 2,5-dicarbomethoxypyrazine, by the freezing point method adapted by Newman,[8] gave an average "*I*" value of 2.55. The acceptance by the solute of an average of 2.55 protons rather than the theoretical maximum of five protons demonstrated the failure of the 2,5-dicarbomethoxypyrazine to undergo the Schmidt reaction.

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(1) From thesis presented in partial fulfillment for the degree of Doctor of Philosophy at the Polytechnic Institute of Brooklyn.

(2) Spoerri and Erickson, THIS JOURNAL, **60**, 400 (1938); Ellingson and Henry, *ibid.*, **71**, 2798 (1949).

(3) McDonald and Ellingson, *ibid.*, **69**, 1034 (1947).

(4) Schaaf and Spoerri, *ibid.*, **71**, 2043 (1949).

(5) Newman, *et al.*, *ibid.*, **63**, 2431 (1941); **70**, 317 (1948).

(6) Smith, *ibid.*, **70**, 320 (1948).

(7) Hammett and Deyrup, *ibid.*, **55**, 1900 (1933); Treffers and Hammett, *ibid.*, **59**, 1708 (1937).

(8) Newman, Kuivila and Garrett, *ibid.*, **67**, 1704 (1945).