ated at 100,000 REP. per hour for 65 hours. Due to the difficulty of isolating butyryl chloride and to avoid heating, the reaction mixture was shaken with ether and extracted with dilute aqueous sodium bicarbonate solution. The alkaline extract was acidified with dilute hydrochloric acid, ether extracted and dried. Evaporation of the ether and distillation of the residue gave a colorless oil (5.6 g.), b.p. 159–161°, $n^{20}D$ 1.3390. The acid gave an anilide, m.p. 96°, that did not depress the melting point of butyranilide. The neutral fraction was dried over anhydrous sodium sulfate and distilled to give butanal and carbon tetrachloride. The residual oil (2.3 g.) on standing liberated hexachloroethane (300 mg.), m.p. 198°, and the oil was shown to be a polymer of butanal.

Analysis of the irradiation product of one of the runs using benzaldehyde (0.4 mole), butanone-2 (0.4 mole) and carbon tetrachloride (0.04 mole) indicated the presence of 8×10^{-4} mole of chloride ion. Assuming that this chloride ion might be present as hydrogen chloride and thus be responsible for an acid-catalyzed system, a run was made using the above concentrations of reagents plus 1.6×10^{-3} mole of trimethylamine. The same condensation products were obtained with the same yields.

Ann Arbor, Mich.

[Contribution No. 493 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Co.]

Syntheses by Free-radical Reactions. IX. Use of Free Radicals from Flames

By C. S. Cleaver, L. G. Blosser and D. D. Coffman

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The free radicals which propagate flames have been used by a novel technique to bring about organic syntheses. The technique involved rapidly passing a stream of aqueous organic reactant through the inner cone of a flame. In this manner, various flames converted aqueous acetic acid to glycolic acid nitrate, succinic, glycolic, hydroperoxyacetic, and chloroacetic acids. These products provided evidence for the abstraction from the flames of nitric oxide and the hydroxyl, hydroperoxy and chlorine-free radicals to effect syntheses. Similar transformations occurred when solutions of pivalic acid, propionic acid, *t*-butylamine and *t*-butyl alcohol were passed through flames.

A novel technique has been devised by means of which the propagating free radicals of flames have been used stoichiometrically to bring about organic syntheses. Flames with temperatures in excess of 800° were employed. The technique involved rapidly passing normal to the flame path, but through or near to the inner cone of the flame (see Fig. 1) an aqueous stream containing in solution an organic reactant. The aqueous stream apparently behaved as a cold wall of solvent which continuously extracted from the flame the free radicals which then reacted with the organic solute.

Synthesis in Flames.—The products isolated after an aqueous solution of an organic reactant had been passed through the inner cone of a methane-oxygen or hydrogen–oxygen flame are listed in Table I. *t*-Butyl alcohol and *t*-butylamine gave $\alpha,\alpha,\alpha'\alpha'$-tetramethyltetramethylene glycol and $\alpha,\alpha,\alpha',\alpha'$-tetramethyltetramethylenediamine, respectively, the products from dehydrogenative coupling reactions. Pivalic acid and propionic acid gave $\alpha,\alpha,\alpha',\alpha'$-tetramethyladipic acid and C_6-dibasic acids, respectively, also by the coupling reaction. Other products from pivalic and propionic acids included the hydroxy and hydroperoxy derivatives. Acetic acid gave exactly analogous products; namely, succinic acid, glycolic acid and hydroperoxyacetic acid. Acetaldehyde and other carbonyl products were formed in minor quantities. Hydrogen peroxide was identified as a product after passage of either water or aqueous acetic acid through a flame.

The formation of the coupled products can be accounted for in terms of the chemistry of hydroxyl radicals which are known to propagate flames[1] and which evidently attacked the organic reactant during passage through the flame. Thus, $\alpha,\alpha,\alpha',\alpha'$-tetramethyltetramethylenediamine from *t*-butylamine, $\alpha,\alpha,\alpha',\alpha'$-tetramethyltetramethylene glycol from *t*-butyl alcohol, $\alpha,\alpha,\alpha',\alpha'$-tetramethyladipic acid from pivalic acid, C_6-dibasic acids from propionic acid, and succinic acid from acetic acid are products typical of the oxidative coupling effected

Table I

Products from Various Reactants Passed Through a Flame

Aqueous organic reactant	Products
t-Butyl alcohol (4%)[a]	$\alpha,\alpha,\alpha',\alpha'$-Tetramethyltetramethylene glycol[i] and resin
t-Butylamine sulfate (13%)[b]	$\alpha,\alpha,\alpha',\alpha'$-Tetramethyltetramethylenediamine[j]
	2,2,5,5-Tetramethyldihydropyrazine[k]
	Unidentified materials containing oxygen and nitrogen
Sodium pivalate (25%)[b]	$\alpha,\alpha,\alpha',\alpha'$-Tetramethyladipic acid[c]
	Hydroperoxypivalic acid[d]
	Hydroxypivalic acid[e]
Propionic acid (2%)[a]	C_6-Dibasic acids[f]
	α- and β-Hydroperoxypropionic acids[g]
	Lactic and hydracrylic acids[h]
Acetic acid (2%)[a]	Succinic acid[l]
	Glycolic acid[l]
	Hydroperoxyacetic acid[l]
	Hydrogen peroxide[m]

[a] H_2/O_2 flame (1:1). [b] CH_4/O_2 flame (1:2). [c] Identified by m.p., mixed m.p., compositional analyses, neut equiv. [d] Identified by reduction to hydroxypivalic acid, peroxide test. [e] Identified by m.p., mixed m.p., C + H analyses, neut. equiv. [f] Probable mixture of adipic, α,α'-dimethylsuccinic and α-methylglutaric acids; identified by comparison of peak elution volumes. [g] Identified by peroxide test. [h] Identified by comparison of peak elution volumes. [i] Identified by X-ray diffraction pattern comparison with authentic material. [j] Identified by C + H analysis, b.p., neut. equiv. [k] Identified by C + H analyses, m.p. [l] See Experimental section for method of identification. [m] Identified by titration with permanganate, ceric, and by iodometric techniques.

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(1) B. Lewis and G. von Elbe, "Combustion, Flames, and Explosions of Gases," Academic Press, Inc., New York, N. Y., 1951.

by hydroxyl radicals[2] as represented by equations a and b

$$HO\cdot + RH \longrightarrow R\cdot + H_2O \qquad (a)$$

$$2R\cdot \longrightarrow R{-}R \qquad (b)$$

Although hydrogen peroxide was formed as a coproduct in many of the experiments, it did not function as a source of hydroxyl radicals for the coupling reaction. This was demonstrated by the passage of aqueous acetic acid–hydrogen peroxide mixtures through the flame. In each instance only the usual products were obtained in about the same quantities as were formed by passage of aqueous 2% acetic acid alone (Table III), and the added hydrogen peroxide was not consumed during passage through the flame.

The precise modes of formation of the hydroxy derivatives of pivalic, propionic and acetic acids are not known, but they almost certainly involved free-radical reactions. The hydroxy derivatives may have originated by combination of R· and HO· or by reduction of peroxy or hydroperoxy compounds during subsequent manipulation.

The formation of hydroperoxy derivatives of pivalic, propionic and acetic acids may have involved the action of hydroperoxy radicals ($HO_2\cdot$) or oxygen on the radical R· of reaction a

$$HO_2\cdot + R\cdot \longrightarrow HO_2R \qquad (c)$$

$$O_2 + R\cdot \longrightarrow ROO\cdot \qquad (d)$$

$$ROO\cdot + H\cdot \longrightarrow ROOH \qquad (e)$$

$$ROO\cdot + RH \longrightarrow ROOH + R\cdot \qquad (f)$$

Effect of Flame Components on Products.—A comparison of the products resulting from passage of aqueous 2% acetic acid through various flames was made (Table II). The H_2/O_2 and CH_4/O_2 flames were approximately equivalent in ability to give succinic, glycolic and hydroperoxyacetic acids. In comparison with these flames, the CO/O_2 flame yielded significantly lesser quantities of succinic and glycolic acids but approximately equal quantities of hydroperoxyacetic acid. The passage of aqueous 2% acetic acid at *p*H 6–8 through flames containing nitric oxide or its precursors gave glycolic acid nitrate as a major product. The formation of glycolic acid nitrate probably involved free radical reaction of an oxide of nitrogen and not spontaneous esterification of glycolic acid by nitric acid, since this esterification does not occur at *p*H 6-8. A source of chlorine in the flame components usually resulted in the formation of chloroacetic acid as the sole product.

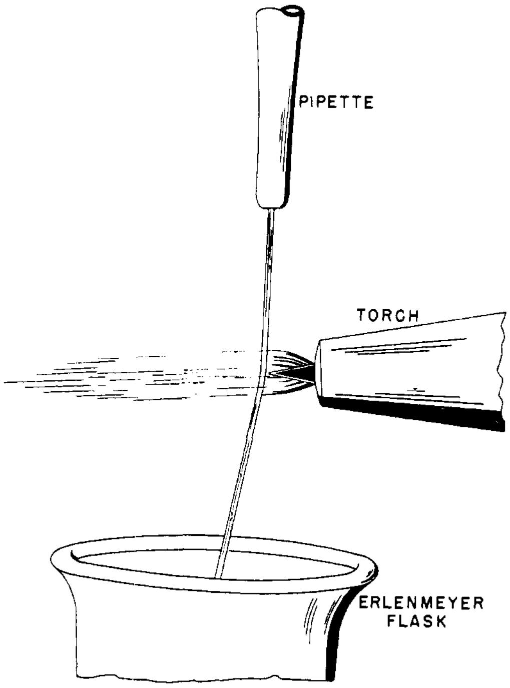

Fig. 1.

Effect of Inorganic Ions on Free Radical Reactions.—Various salts, hydrogen cyanide and hydrogen peroxide were added to aqueous solutions of acetic acid prior to passage through a H_2/O_2 flame. The results obtained in the presence of sodium acetate (see Table III) suggest that sodium ions and the *p*H of the solution were without major effect on the products formed from acetic acid. Chloride ions caused formation of chloroacetic acid and decreased the yields of the usual products. Bromide ions at high concentrations inhibited the formation of all products. At lower concentrations, bromoacetic acid and traces of the other usual products were formed. Fluoride ions were without effect, and fluoroacetic acid was not formed. Sodium cyanide, sodium sulfide and lead acetate inhibited the formation of coupled, hydroxy, and hydroperoxy products, possibly because these easily oxidizable substances destroyed the radicals before reaction with the organic substrate could occur. Dissolved ceric IV ion and SO_2 inhibited the formation of hydroperoxyacetic acid without altering greatly the succinic and glycolic acid synthesis.

Formation of the halogenated acids probably proceeded according to equations g and h when aqueous acetic acid containing sodium chloride or sodium bromide was passed through a flame.

$$HO\cdot + X^- \longrightarrow HO^- + X\cdot \qquad (g)$$

$$X\cdot + \cdot CH_2COOH \longrightarrow XCH_2COOH \qquad (h)$$

This same mechanism may have been operative when aqueous acetic acid initially free of halide sources was passed through flames containing a halogen source. *e.g.*, a methyl chloride/oxygen flame (see Table II). The aqueous solution was found to absorb hydrogen chloride formed by combustion. This halogen acid may have been the source of chloride ion and radicals for reactions g and h.

Concentration of Organic Reactant.—Water was found necessary as a carrier for the organic reactant. Thus, when anhydrous acetic acid was passed through reducing and oxidizing flames from H_2/O_2 and CH_4/O_2, only traces of products were formed, and 93% of the acetic acid was recovered. The effect of intermediate concentrations of aqueous organic reactant on product formation was examined by passing 2, 25 and 50% solutions of propionic acid through a 1:1 H_2/O_2 flame. The quantities of C_6-acids formed were 50, 210 and 120 mg., respectively. Propionic acid alone gave 1

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[2] D. D. Coffman, E. L. Jenner and R. D. Lipscomb, THIS JOURNAL, **80**, 2864 (1958).

TABLE II

EFFECT OF VARIOUS FLAMES ON TRANSFORMATIONS OF ACETIC ACID[g]

	Acidic products, mg.			
Flame	Succinic	Glycolic	Hydroperoxyacetic	Others
H_2/O_2 (1:1)	16	10	22	[a,h]
H_2/O_2 (6:1)	6	3	18	[a]
CH_4/O_2 (1:3)	10	11	85	[a,b,h]
NH_3/O_2 (1:1.25)	0.5	0.8	0.0	5.2 glycolic acid nitrate[c]
CO/O_2 (2:1)	3.0	5	29	[a,h]
$NH_3/H_2/O_2$ (1:8:5)	4.1	2.0	2.8	10 glycolic acid nitrate[c]
$H_2/O_2/NO$ (5:2:1)[d]	16	21.2	0	146 glycolic acid nitrate[a,e,c]
$H_2/O_2/NO_2$ (6:3:1)[d]	20	27	97	25.4 glycolic acid nitrate[a,c]
HCN/O_2 (0.6:1)[d]	10	7	14	4 glycolic acid nitrate[c]
H_2/Cl_2 (1.3:1)	0	0	0	27 chloroacetic acid[f]
CH_3Cl/O_2 (1:2)[d]	0	0	0	64 chloroacetic acid[f]
$H_2/O_2/HCl$ (1:1:0.03)	1.2	5.1	21.3	50 chloroacetic acid[a,f]
$H_2/H_2S/O_2$ (1:0.1:1)	0.6	0.4	0	Sulfur
$H_2/SO_2/O_2$ (1:0.1:1)	5.6	2.2	8.7	

[a] Unidentified acid with peak elution volume between acetic and succinic acid; minor amounts. [b] Unidentified acid with peak elution volume identical to propionic acid; minor amounts. [c] Identified by comparison of peak elution volumes and infrared spectra with authentic sample. [d] 4% Aqueous acetic acid passed through flame. [e] Unidentified acid with peak elution volume identical to hydroperoxyacetic acid; non-peroxidic. [f] Identified by comparison of peak elution volumes with authentic acid. [g] Aqueous 2% acetic acid (300 ml.) was passed through the flame 10 times. [h] Hydrogen peroxide.

TABLE III

EFFECT OF INORGANIC IONS IN SOLUTION ON TRANSFORMATIONS OF ACETIC ACID[a,b]

	Acidic products, mg.			
Aqueous solution	Succinic	Glycolic	Hydroperoxyacetic	Others
0.33 *M* acetic acid	16	10	22	
.33 *M* sodium acetate	21.8	9.3	21.8	
.33 *M* acetic acid .16 *M* hydrogen peroxide	4.3	8.2	31.0	
.33 *M* acetic acid 1.0 *M* sodium chloride	2.6	3.6	7.0	43 chloroacetic
0.66 *M* acetic acid .20 *M* sodium bromide	Trace	Trace	Trace	19 bromoacetic
.33 *M* acetic acid 1.0 *M* sodium fluoride	20.0	2.9	7.4	
0.33 *M* acetic acid 1.0 *M* hydrogen cyanide	20.0	43	73	
0.33 *M* acetic acid .125 *M* ceric sulfate	6.7	11.5	0.0	White ppt.

[a] H_2/O_2 (1:1) flame used throughout. [b] Aqueous 2% acetic acid (300 ml.) was passed through flame 10 times.

mg. of C_6-acids. Thus, the quantities decreased rapidly when the concentration of propionic acid increased above 25%. Aqueous solutions of acid salts or amine salts decreased the volatility of the organic substrates and were operable at higher concentrations than were solutions of the free acids or amines. Only traces of products were formed when 2% solutions of acetic acid in concentrated sulfuric acid or in tetrachloroethylene were passed through an H_2/O_2 flame.

The unique ability of water to function as the carrier for the organic reactant may be partly dependent upon its high heat of vaporization and non-combustibility. Thus, carriers with lower heats of vaporization may have formed surface layers of vapor which impeded passage of free radicals from the flame into the carrier liquid. Also, the hydroxyl radical and radicals considered *less reactive* than the hydroxyl radical, such as NO, $HO_2\cdot$ or $Cl\cdot$, may have existed in aqueous solution for appreciable periods of time before destruction. However, radicals considered *more reactive* than the hydroxyl radical, such as the fluoride radical, may have been short lived in aqueous solutions because of a degenerative reaction such as i.

$$F\cdot + H_2O \longrightarrow HF + HO\cdot \qquad \text{(i)}$$

Thus, evidence for reactions in which $\cdot F$ participated was not obtained, and reactions typical of its degradation product, the hydroxyl radical, were observed (see Table III). The cyanide radical may have been destroyed oxidatively or hydrolytically and its participation in the reactions was not noted.

Lifetime of the Free Radicals and Location of the Highest Concentration of Radicals in Flames.— Brief explorations indicated the preferred rates of liquid injection, flame compositions and areas within the flame most effective with respect to the availability of free radicals. The amounts of hydrogen peroxide or iodine found after passage of distilled water or dilute potassium iodide solutions through the flame were arbitrarily chosen as criteria of the effectiveness of radical extraction from the flame. Hydrogen peroxide was determined by standard permanganate, ceric or iodometric titrations. Iodine was determined by titration with standard thiosulfate.

To place the experiments with water and potassium iodide solutions on a comparable basis, the results have been expressed in terms of milliequivalents of titratable oxidant formed in one liter of solution in a single pass through the flame. Figures 2, 3, 4 and 5 summarize the results and indicate that optimum extraction of radicals occurred with oxidizing flames (Fig. 2) through which the stream passed close to the inner cone (Fig. 3) at slow flow-rates (Fig. 4). The total quantity of fuel and oxidant supplied to the flame was relatively unimportant (Fig. 5). Higher values of titratable oxidant were obtained using iodide solutions (Fig. 2) than were obtained with water alone. Thus, the reaction yielding iodine was more efficient in capturing radicals than was the reaction yielding hydrogen peroxide.

Other experiments suggested that the *lifetime* of the radicals in the aqueous solution was less than 0.006 second. A stream of distilled water was passed through the flame and mixed with a stream of potassium iodide 0.006 second after exit from the flame. The amount of iodine immediately liberated corresponded to the amount of hydrogen peroxide that was found after passing a like volume of water through the flame at the same rate and later analyzing for the hydrogen peroxide

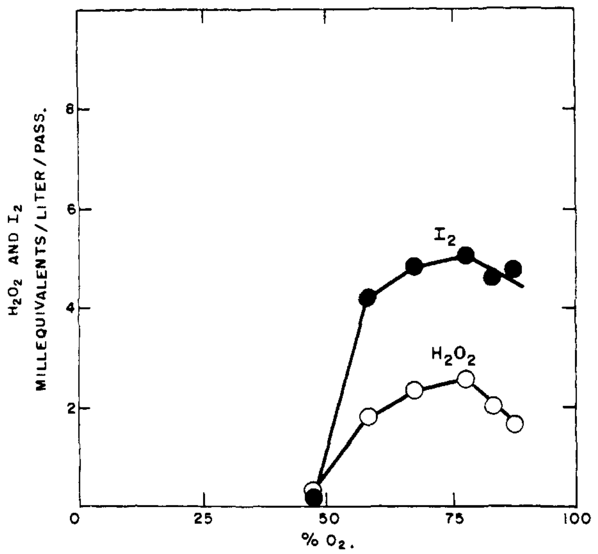

Fig. 2.—Effect of flame composition on amount of hydrogen peroxide and iodine formed in aqueous streams; flame, city gas/oxygen.

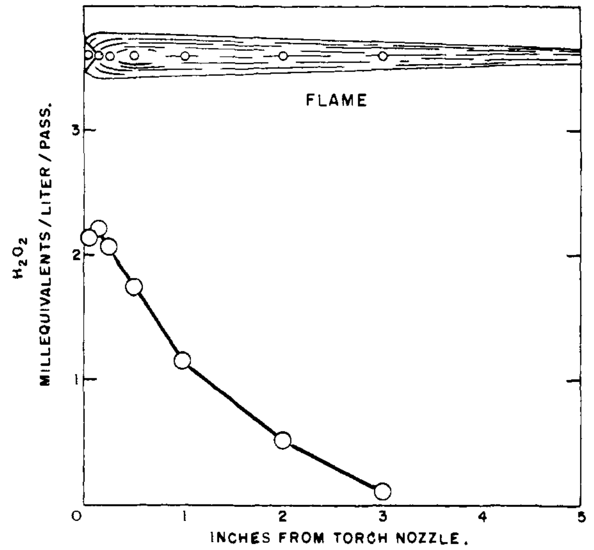

Fig. 3.—Effect of distance from inner cone on amount of hydrogen peroxide formed in aqueous stream; flame composition: 1/3.1 city gas/O$_2$.

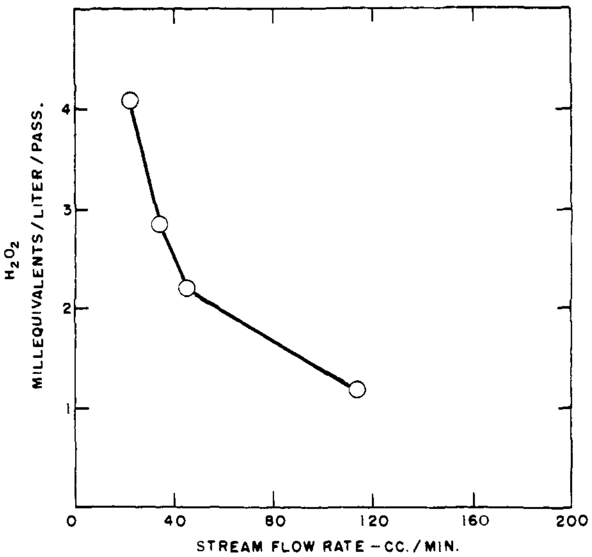

Fig. 4.—Effect of rate of injection of stream through flame on amount of hydrogen peroxide formed in aqueous stream; flame composition: 1/3.1 city gas/O$_2$.

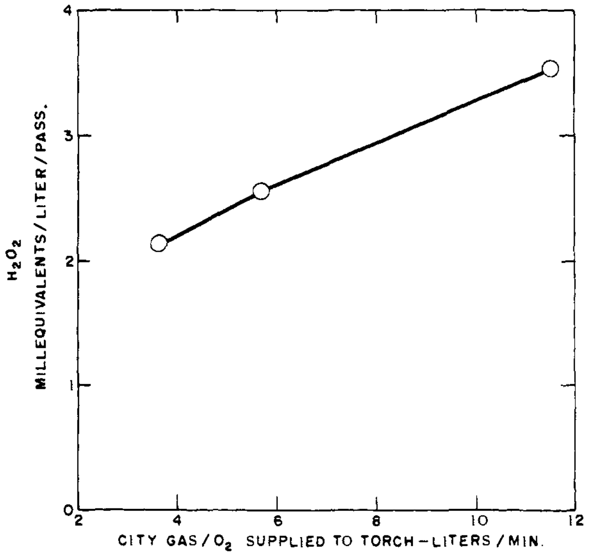

Fig. 5.—Effect of flame size on amount of hydrogen peroxide formed in aqueous stream; flame composition: 1/3.1 city gas/oxygen.

content by permanganate oxidation. Thus, unreacted radicals were not present when the aqueous stream from the flame was passed into potassium iodide solution, and the radical lifetime must have been less than 0.006 second.

Essentially no hydrogen peroxide was formed when reducing flames were used (Fig. 2), while the organic transformations occurred in fair yields (Table II, reducing H$_2$/O$_2$ flame). It thus appears that the formation of hydrogen peroxide does not necessarily require hydroxyl radicals. This is additional evidence for the non-participation of hydrogen peroxide in the organic transformations.

A Multiple Stream Reactor.—A multiple stream reactor fashioned in principle after the single stream apparatus was more efficient in abstracting free radicals from the flame. Thus, a fivefold increase in the amount of hydrogen peroxide synthesized per mole of methane consumed was achieved by passing from a spinnerette an array of twelve fine streams (rather than a single stream), each 0.16 mm. in diameter, through a $^1/_4$-inch wide 1:2.7 CH$_4$/O$_2$ flame.

A still greater number of streams arranged in parallel rows before the flame were more efficient than the twelve-stream apparatus in abstracting free radicals from the flame, but the efficiency did not increase in proportion to the number of streams. Thus eighty-four streams (each 0.006″ in diameter and 0.012″ apart), arranged in four rows 0.01″ apart, were only ten times as effective in abstracting free radicals from the flame as was the single stream as judged by the amount of hydrogen peroxide formed per mole of methane consumed. However, the 84-stream arrangement was eighteen times as effective as the single stream when a pressure gradient was applied across the streams to force movement of the flame gases over the streams. This forced draft arrangement also gave ten times the quantities of succinic, glycolic and hydroperoxyacetic acids per liter of methane consumed compared to the single stream apparatus when aqueous 2% acetic acid was passed through the flame.

Experimental

1. **Flame Reactor and Reaction Technique. Torches.**—Two torches were used for the majority of experiments. The National 3A Blow Pipe with an OX-3 or OX-5 nozzle maintained the flames of premixed fuel components. A torch with a small stainless steel nozzle was fabricated for experiments involving hazardous combustion mixtures. In this torch, the fuel was supplied through a cluster of four small stainless steel tubes to the face of the torch. The oxidant was supplied to the interstices surrounding the tubes at the face of the torch. The geometry of the torch face resembled four circles encompassed by a square.

Gas Metering.—The gaseous fuels and oxidants were metered to the torches through Fischer and Porter flowrators containing the appropriate precision-bored tube. Corrections for various gas densities were made by calibration with wet-test meters or by use of Graham's law. Liquid fuels (b.p. <100°) were supplied at known rates to the torches either from "constant head" burets or by mercury displacement from graduates. The liquid was subsequently vaporized in a steam-heated coil and was supplied through steam-heated lines to a torch wrapped in steam-heated copper tubing.

Solution Injection.—The aqueous organic reactant was usually fed to and issued from a 1-ml. pipet having a nozzle of 0.022 inch inside diameter (Fig. 1). The pipet was connected to an elevated 500-ml. buret. Flow-rates of the aqueous organic reactant were controlled by raising or lowering the buret or by manipulating the stopcock of the buret. The solution was collected in an ice-cooled erlenmeyer flask. As illustrative of operating conditions, a solution flow-rate of 50 ml./min. caused the jet of aqueous organic reactant to pass through a 1-cm. thick flame with a contact time of *ca.* 0.003 second. The stream issued from the flame with a mean temperature of 35°. The solution was recycled by transfer from receiver to buret at the end of each pass.

2. **Products from Aqueous Acetic Acid.**—A representative experiment involving radical attack on acetic acid is as follows: Aqueous 2% acetic acid (6.0 g. of acid in 300 ml. of distilled water) was passed 10 times through the tip of the inner cone of a 1:1 hydrogen/oxygen flame at the rate of 50 ml./min. The solution was placed in a continuous liquid-liquid ether extractor for 48 hours to separate the organic acids almost quantitatively. The ether extract was dried over magnesium sulfate, and the drying agent was filtered from solution. The filtrate was then gently heated on a steam-bath to remove most of the ether. A fraction of the total residue was chromatographed for an indication of the total number of volatile and non-volatile acidic components. The residue was concentrated either *in vacuo* at room temperature or by a stream of nitrogen at 60° to remove unreacted acetic acid, and the total concentrate was then chromatographed.

The organic acids were chromatographed by modifications of the technique described by Marvel and Rands.[3] Two methods were employed, each using 25 g. of silicic acid to facilitate the separation of larger quantities of acids. In method I, the column was prepared with an 85:15 chloroform-butanol solution, and elution was started with 85:15 chloroform–butanol solutions, followed by 80:20, 75:25, etc. This method was used for rapid separation and identification of acids of low distribution coefficients in chloroform–water systems. Method II, starting with 100% chloroform, followed by 95:5, 90:10 chloroform–butanol, etc., was used to separate mixtures containing acids with high distribution coefficients in chloroform–water systems. Peak elution volumes for the acids pertaining to this study are given in Table IV. Several acids were also isolated and identified by means of melting points, analysis or X-ray diffraction patterns. Other products were only tentatively identified by a comparison of their peak elution volumes. It has not yet been possible to assign structures to a few acids synthesized as minor percentages of the products.

TABLE IV

PEAK ELUTION VOLUMES OF ACIDS (ML.)

Acids	Method I[a]	Method II[b]
Pivalic		30–40
α,α,α′,α′-Tetramethyladipic		130–150
Propionic	20–30	150–170
Bromoacetic	30–40	160–170
Glycolic acid nitrate	30–50	180–200
Chloroacetic	30–50	180–190
Acetic	60–70	220–230
Glutaric	80–90	(340–350)[c]
Formic	140–150	(310–330)[c]
Succinic	180–190	(460–480)[c]
Hydroperoxypivalic		230–240
Hydroperoxyacetic	240–260	
Hydroxypivalic		250–270
Malonic	250–280	
C_6 dibasic acids		260–280
α-Hydroperoxypropionic		380–400
Glycolic	420–450	
Lactic		440–470
β-Hydroperoxypropionic		460–480

[a] 25 g. of silicic acid prepared in 85:15 chloroform-butanol solution. [b] 25 g. of silicic acid prepared in 100% chloroform solution. [c] Not in consecutive order.

It was observed that the partition chromatographic technique likewise separated peroxidic components. The fractions containing peroxides were discovered after titration for acidic components by adding a few ml. of 2% potassium iodide solution to each neutralized fraction followed by a few ml. of starch solution. The characteristic starch–iodine color in several fractions indicated the presence of peroxides. When a peroxide occurred in fractions which also contained acids, the peroxide was reduced to a non-peroxidic acid for subsequent identification. Several peroxides were non-acidic and were not identified.

Chromatography of the concentrate from the acetic acid experiment by method I afforded the results shown in Fig. 6-A. In addition, positive peroxide tests were observed at 60–70 ml., 90–110 ml. and 240–280 ml. (not shown in Fig. 6-A). The neutralized aqueous layer of peroxidic fraction 250–260 ml. from another identical experiment was reduced with 15 mg. of sodium sulfite at 25° for 15 hours, acidified, continuously ether-extracted for 15 hours, worked up and chromatographed (Fig. 6-B). A mixture of authentic acetic, succinic and glycolic acids was chromatographed (Fig. 6-C). Figure 6-A indicated that, in addition to acetic acid, three other acids were present in the flame-treated solution, and the starch–iodine tests suggested that one (acid X) was peroxidic. A comparison of Fig. 6-A with Fig. 6-C suggested that two of the acids were succinic and glycolic acids. Figure 6-B proved that the peroxidic acid could be reduced by sodium sulfite to a non-peroxidic acid with a peak volume identical to that of glycolic acid. Since reduction by sodium sulfite is characteristic of hydroperoxides,[4] and since concentrated solutions of the peroxidic acid evolved gas when treated with lead tetraacetate which is also a characteristic test for hydroperoxides,[5] the peroxidic acid is believed to be the hitherto unknown hydroperoxyacetic acid. The peroxides at 60–70 ml. and 90–110 ml. were not identified. A minor acidic component at 140–160 ml. was not identified. The amounts of the three identified acids formed in this experiment were calculated to be 16 mg. of succinic, 22 mg. of hydroperoxyacetic and 10 mg. of glycolic acids. Chromatography by means of method II revealed minor amounts of another acid with a characteristic peak elution volume identical to that for propionic acid.

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(3) C. S. Marvel and R. D. Rands, Jr., THIS JOURNAL, **72**, 2642 (1950).

(4) H. Hock and S. Lang, *Ber.*, **74**, 313 (1942).

(5) R. Criegee, *ibid.*, **72**, 1799 (1939).

In other identical experiments, it was observed that ketones and aldehydes were products, since a precipitate formed in the flame-treated aqueous acetic acid when 2,4-dinitrophenylhydrazine was introduced after the manner of Cavallini, *et al.*[6] The precipitate was filtered, dried, and chromatographed as follows: Twenty-five grams of silicic acid (Mallinckrodt, specially prepared for chromatographic analysis by the method of Ramsey and Patterson) was slurried without further treatment with 100 ml. of hexane (Ansco *n*-hexane, American Mineral Spirits Co., 230 N. Michigan Ave., Chicago, Ill.) in an erlenmeyer flask. The slurry was then added to a 2.5 × 43 cm. column fitted with a sintered glass disk at the bottom and a removable three-way stop-cock at the top. The supernatant hexane was forced from the tube by nitrogen pressure through the three-way stop-cock until the column became firm, but not dry or cracked. The mixture of 2,4-dinitrophenylhydrazones (0.5–20 mg., depending on the number of components) was dissolved in 5 ml. of reagent benzene, applied to the column, and washed on with two 2-ml. portions of benzene. Development and elution was carried out by consecutive 100-ml. portions of each of the following hexane–anhydrous diethyl ether mixtures: 95:5, 90:10, 85:15, 80:20, etc. As each colored zone was eluted from the column, the total volume was noted and compared with peak elution volumes of authentic samples of 2,4-dinitrophenylhydrazones. Peak elution volumes determined for 2,4-dinitrophenylhydrazones important in this investigation are given in Table V. More than twelve colored fractions were observed as products from the flame-treated acetic acid solution (Table V, column A).

The colors of several fractions were atypical of ordinary 2,4-dinitrophenylhydrazones and may have been oxidized derivatives of the 2,4-dinitrophenylhydrazones from the action of hydroperoxides or hydrogen peroxide on the original 2,4-dinitrophenylhydrazones. This was partially confirmed by adding sodium sulfite to a flame-treated solution of acetic acid before adding the 2,4-dinitrophenylhydrazine solution. Chromatography of a precipitate prepared in this fashion indicated fewer colored components (Table V, B). A comparison with authentic peak elution volumes suggested the presence of the 2,4-dinitrophenylhydrazones of acetaldehyde, glyoxal and pyruvic acid, and several unidentified 2,4-dinitrophenylhydrazones. The quantities of aldehydes and ketones formed were minor with respect to succinic, hydroperoxyacetic and glycolic acids.

TABLE V

PEAK ELUTION VOLUMES OF 2,4-DINITROPHENYLHYDRAZONES (ML.)

Carbonyl compound	Authentic peak elution volumes[a]	A Flame synthesized compounds[b]	B Flame synthesized compounds (Na_2SO_3)[b]
Diethylketone	170–190		
Propionaldehyde	220–250		
		310–325	
Acetone	320–340	330–345[c]	
Acetaldehyde	350–380	370–390	355–370
Formaldehyde	410–440	410–440	
		470–500[d]	
Biacetyl	560–590	540–570[e]	
		650–700	650–700
Glyoxal	760–790	730–760	750–775
		830–860	850–875
Pyruvic acid	860–910	900–950	935–980
		1020–1070[f]	1120–1160
		1150–1200	

[a] All compounds in the column were yellow. [b] From acetic acid. [c] Orange. [d] Lavender. [e] Orange-brown. [f] Pink.

3. **Multiple Stream Reactions.**—The 84-stream nozzle with a pressure gradient across the streams was used to convert aqueous sodium pivalate and aqueous *t*-butylamine to products in quantities sufficiently large to permit use of standard isolation and identification techniques. The solutions were recycled through the flame by means of a Viking ECH-2 steel gear pump. The solution passed through a filter pack consisting of five layers of glass cloth and two layers of viscose filter cloth housed in a stainless steel pipe coupling just before issuing from the spinnerette. The streams were cooled before recirculation by passing through an ice-cold Graham condenser.

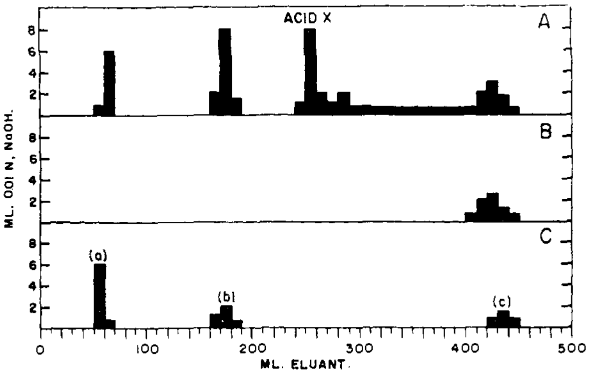

Fig. 6.—Chromatographic identification of products from acetic acid: A, acetic acid through flame; B, acid "X" after treatment with Na_2SO_3; C, authentic mixture of (a) acetic, (b) succinic and (c) glycolic acids.

With Sodium Pivalate.—By this technique, a liter of aqueous sodium pivalate (*p*H *ca.* 10.0) containing 200 g. of pivalic acid was pumped through a methane/oxygen flame for 4 hours at the rate of 800 ml./min. During this time, the flame consumed 187 l. of methane and 500 l. of oxygen. Chromatography of a small fraction of the solution indicated the presence of 17.7 g. of $\alpha,\alpha,\alpha',\alpha'$-tetramethyladipic acid, 15.0 g. of hydroxypivalic acid, 17.5 g. of hydroperoxypivalic acid, 8.0 g. of unidentified acids, and 120 g. of unreacted pivalic acid in the total solution. These products accounted for 170 g. of the original 200 g. of pivalic acid. The literature[1] indicated that 19.6 g. of gaseous hydroxyl radicals had been formed by the methane/oxygen flame during the reaction, and the amounts of products formed indicated that about 55% of these radicals were abstracted from the flame and utilized in effecting the syntheses.

The total solution was treated with 20 g. of sodium sulfite to reduce peroxides. After 18 hours, the solution was acidified with 70 ml. of concentrated sulfuric acid. Steam distillation of the acid solution, followed by ether extraction of the distillate and fractionation of the extract yielded 95.0 g. of unreacted pivalic acid, b.p. 160–161°, and 3.0 g. of unidentified higher boiling material. From the cooled aqueous acid solution remaining after steam distillation there was obtained by filtration 12.0 g. of crude $\alpha,\alpha,\alpha',\alpha'$-tetramethyladipic acid, m.p. 170–189°. Three recrystallizations from aqueous acetic acid yielded 6.9 g. of $\alpha,\alpha,\alpha',\alpha'$-tetramethyladipic acid, m.p. 191–193°.

Anal. Calcd. for $C_{10}H_{18}O_4$: C, 59.4; H, 8.92; neut. equiv., 101. Found: C, 58.1; H, 9.09; neut. equiv., 101.

A fraction of the aqueous filtrate was chromatographed. The chromatograph indicated that 8.0 g. of $\alpha,\alpha,\alpha',\alpha'$-tetramethyladipic acid, 24.0 g. of hydroxypivalic acid and about 8.0 g. of unidentified acids remained in solution after initial removal of the $\alpha,\alpha,\alpha',\alpha'$-tetramethyladipic acid. The total solution was continuously ether extracted for 24 hours, and the extract was fractionated in a short still. There was obtained 15 g. of crude hydroxypivalic acid as white crystals, b.p. 115–120° (1 mm.), m.p. 74–84°, neut. equiv., 121. Four recrystallizations from toluene–acetone mixtures followed by sublimation yielded 10 g. of hydroxypivalic acid, m.p. 123–125°.

Anal. Calcd. for $C_5H_{10}O_3$: C, 50.8; H, 8.47; neut. equiv., 118. Found: C, 50.3; H, 8.60; neut. equiv., 117.

The other acids which were present in smaller amounts were not isolated in pure condition.

With *t*-Butylamine Sulfate.—Two hundred grams of *t*-butylamine (200 g.) was dissolved in aqueous sulfuric acid to obtain a total volume of 1500 ml. with *p*H of 5.0. This solution was recycled, as already described for the preparation of $\alpha,\alpha,\alpha',\alpha'$-tetramethyladipic acid, through a methane/

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[6] D. Cavallini, N. Frontalli and G. Toschi, *Nature*, **163**, 568 (1949).

oxygen flame for 225 minutes at the rate of 775 ml./min. Thirty grams of sodium sulfite was added to the solution to reduce peroxides. Dilute sodium hydroxide was added to raise the *p*H to 7.0, and the solution was ether extracted continuously for 72 hours. From the ether extract there was obtained 3 g. of crude 2,2,5,5-tetramethyldihydropyrazine. After recrystallization from diethyl ether-petroleum ether mixtures, the crystals melted at 82-84°.

Anal. Calcd. for $C_8H_{14}N_2$: C, 69.6; H, 10.14; N, 20.23. Found: C, 69.57; H, 10.47; N, 20.17.

The aqueous layer was concentrated *in vacuo* to a volume of 200 ml. Solid potassium hydroxide (1.36 kg.) was added, and the solution was ether extracted batchwise with 1.36 kg. of ether. The ether extract was dried over solid potassium hydroxide and was distilled to yield a low boiling ether-*t*-butylamine azeotrope and 18 g. of higher boiling material, b.p. 80° (25 mm.) to 110° (5 mm.), and 5 g. of crude crystalline 2,2,5,5-tetramethyldihydropyrazine. Careful distillation of the higher boiling liquid fraction in a small spinning band column yielded the fractions shown in Table VI. Additional experimental details may be found in the patents listed below.[7]

TABLE VI

DISTILLATION OF HIGH BOILING AMINE FRACTION

Fraction	Ml.	B.p., °C., at 10 mm.	Analyses, % C	H	N	O^a	Neut. equiv.
1	2.7	72–73					
2^c	3.0	73–73.5	59.8	13.0	16.3	10.9	80.0
3^c	3.8	74–75.5	60.8	13.4	16.6	9.2	80.3
4	0.64	75.0–75.5					
5^b	2.0	76–78	64.6	13.8	17.8	3.8	75.5
6	1.1	80–107					
7	0.3	112.5–112.5					
8	1.5	118–135	62.4	12.1	17.2	8.3	84.0
9	0.3	135–133					

[a] By difference. [b] Fraction 5 is impure $\alpha,\alpha,\alpha',\alpha'$-tetramethyltetramethylenediamine. *Anal.* Calcd. for $C_8H_{20}N_2$: C, 66.2; H, 13.9; N, 19.5; neut. equiv., 72. [b,c] Fractions 2 and 3 appear to be very impure β-hydroxy-*t*-butylamine, probably contaminated by $\alpha,\alpha,\alpha',\alpha'$-tetramethyltetramethylenediamine. *Anal.* Calcd. for $C_4H_{11}NO$: C, 53.9; H, 12.4; N, 15.7; neut. equiv., 89. The other fractions have not been identified.

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[7] (a) C. S. Cleaver, U. S. Patent 2,782,219, issued February 19, 1957; (b) U. S. Patent 2,833,822, issued May 6, 1958.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE GEORGIA INSTITUTE OF TECHNOLOGY]

Polar Effects on Rates and Equilibria[1]

BY JACK HINE

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By assuming only the applicability of a linear free energy relationship like the Hammett equation, except that the *meta* and *para* reaction constants need not be identical, an equation is derived to show that the reaction constant for an equilibrium process divided by the difference between the substituent constants for the two groups being equilibrated yields a constant, τ_{meta} or τ_{para}, that is independent of the nature of the reaction, but which may vary with the solvent and temperature. From this relationship it is possible to calculate a reaction constant for any equilibrium for which the requisite substituent constants are available and, by application to rate processes, to calculate substituent constants for transition state groupings. By making the Hammett equation assumption that *meta* and *para* reaction constants are identical. equations are obtained that are clearly inconsistent with the substituent constants obtained from the defining reaction, the ionization of benzoic acids. It therefore follows that the Hammett equation could not possibly be *generally* applicable to equilibrium constants of *m*- and *p*-substituted benzene derivatives. Assuming, however, that the Hammett equation does hold, values of τ_m and τ_p are calculated from data on the acidity of benzenedicarboxylic acids, diols and diamines. The results show satisfactory internal consistency and each value is around 3.0.

Introduction

If the Hammett equation[2,3] is applicable to the reaction series

$$ArX_1 \rightleftarrows ArX_2 \qquad (1)$$

where ArX_1 is the reactant and ArX_2 represents the product in an equilibrium process or the transition state in a rate process, then for the rate or equilibrium constants obtained one may write

$$\log \frac{K^x}{K^x_0} = \rho_x\sigma \qquad (2)$$

where K^x_0 is the rate or equilibrium constant for the unsubstituted compound, K^x is the value for a *m*- or *p*- substituted derivative under the same conditions, σ is a constant that depends on the nature of the substituent, and ρ_x is a constant that depends only on the nature of the reaction, solvent and temperature. The electron-donating or -withdrawing ability of the substituent is measured by σ, and ρ is a measure of the sensitivity of the reaction to changes in the polar character of substituents. A number of workers have pointed out that the sign and magnitude of ρ give valuable information about the difference in polar character between the groups X_1 and X_2. No quantitative relationships between ρ's and other parameters of linear free energy relationships appear to have been reported, however, and in fact, for the related Taft equation it has been stated "The quantitative prediction of ρ^* from theory has not been considered and remains an endeavor for the future."[4a] It is now shown that if the groups X_1 and X_2 in the general reaction 1 can, as substituent groups, be fitted to the Hammett equation (even if the σ's for them hold only for the conditions under which the K^x's are determined), ρ_x will be proportional to the difference between the σ constants of the two groups. The proportionality constants, measures of the effectiveness with which the influence of the substituents is *transmitted* to the reaction center, will be denoted τ. While a τ will have a definite value under a given set of conditions its value may vary with temperature, solvent and ionic strength.

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[1] Presented before the Philadelphia Organic Chemist's Club, May 1, 1958.

[2] L. P. Hammett, *Chem. Revs.*, **17**, 125 (1935); THIS JOURNAL, **59**, 96 (1937); "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chapt. VII.

[3] H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

[4] R. W. Taft in M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956; (a) p. 612, (b) Chapt. 13.