trated sulfuric acid and twice from aluminum amalgam and according to the method of Weaver[16] contained not more than 0.001% water.

Runs which were carried out in sealed tubes were followed usually by estimation of base, using a standard back-titration procedure. End-points were obtained by using mixed brom cresol green–methyl red as indicator.

For 4-chloro-3-nitrofluorobenzene, volumes were withdrawn in duplicate. One of each pair was used to estimate base as above and in the other the concentration of chloride ion was measured potentiometrically. The end-points in the latter case were obtained using a Müller capillary electrode system with silver wire. Equal initial concentrations of base and aromatic compound were used with the fluoro compound but not the others.

Rate constants were obtained from titration values by graphical plots. Values for each temperature are from duplicate runs. In the case of 4-chloro-3-nitro-fluorobenzene the reaction taking place is

$$\mathrm{FArCl} + \mathrm{OMe}^- \longrightarrow \mathrm{FArOMe} + \mathrm{ClArOMe} + \mathrm{F}^- + \mathrm{Cl}^-$$

The rate constant (K) calculated from the rate of disappearance of base is the sum of the rates of displacement of Cl (k_{Cl}) and F (k_{F}), whence the individual values are readily derived.

TYPICAL RUN

Log term	Time, sec.	Log term	Time, sec.	Log term	Time, sec.
0.2061	0	0.2465	600	0.3214	1920
.2093	120	.2522	840	.3485	2280
.2136	240	.2699	1080	.3706	2640
.2205	360	.2832	1320	.3923	3000
.2277	480	.3048	1620		

This leads to a value of $k_2 = (6.789 \pm 0.067) \times 10^{-3}$ liters moles^{-1} sec.$^{-1}$.

Preparation of Materials. 4-Chloro-3-nitroaniline.—From p-chloroaniline by the method of Morgan and Porter[17] except that the reaction was carried out at −15° and the product purified by charcoaling the solution in concd. HCl, precipitating with alkali, then crystallizing from water; yield 53%, m.p. 102° (lit. 102°).

4-Chloro-3-nitrobenzenediazonium Fluoroborate.—By a standard procedure[18]; yield 81%, m.p. 164° dec. This compound has not been previously reported.

4-Chloro-3-nitrofluorobenzene.—By a standard procedure,[18] followed by vacuum distillation; yield 10%, m.p. 38° (lit. 38°).

2,5-Dichloronitrobenzene.—The commercial product was recrystallized to constant melting point from ethanol, m.p. 54° (lit. 54°).

4-Bromo-2-nitroaniline.—From o-nitroaniline by the method of Bradfield, Orton and Roberts[19]; yield 60%, m.p. 109–110° (lit. 111°).

4-Chloro-3-nitrobromobenzene.—From 4-bromo-2-nitroaniline by the Sandmeyer reaction. The product was vacuum distilled and recrystallized from petroleum ether; yield 49%, m.p. 72° (lit. 72°).

4-Chloro-3-nitroiodobenzene.—This was prepared by an adaptation of a method of Derbyshire and Waters[20] used for preparing m-iodobenzoic acid; 16 g. of o-chloronitrobenzene, 16 g. of silver sulfate, 240 ml. of concd. H_2SO_4 and 30 ml. of water were mixed in a 3-necked flask fitted with stirrer. The mixture was heated on a boiling water-bath and 26 g. of finely powdered iodine added over 2–3 hours. Heating and stirring were continued for 15 hours, during which time silver iodide precipitated. After cooling, the reaction mixture was poured onto ice and unreacted iodine destroyed with sodium sulfite. The mixture was extracted with ether, the extract dried and then the ether evaporated off. The product was crystallized from ethanol; yield 54%, m.p. 74.5° (lit. 74.5°). This one step procedure seems superior to other methods in the literature.

Acknowledgment.—Assistance from the Research Grant to Australian Universities is gratefully acknowledged.

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[16] E. R. Weaver, THIS JOURNAL, **26**, 2463 (1914).

[17] G. T. Morgan and J. W. Porter, *J. Chem. Soc.*, **107**, 652 (1915).

[18] "Organic Reactions," Vol. 5, John Wiley and Sons, Inc., New York, N. Y., pp. 119–202.

[19] A. E. Bradfield, K. J. P. Orton and I. C. Roberts, *J. Chem. Soc.*, 784 (1928).

[20] D. H. Derbyshire and W. A. Waters, *ibid.*, 3694 (1950).

NEDLANDS, WESTERN AUSTRALIA

[CONTRIBUTION FROM THE EXPERIMENT STATION, HERCULES POWDER COMPANY]

Mechanisms of Reduction of Cumene Hydroperoxide. I. Reduction by Electron Transfer with Ferrocyanide Ion

BY HAROLD BOARDMAN

RECEIVED FEBRUARY 23, 1953

Cumene hydroperoxide is reduced by a one-electron transfer to the α,α-dimethylbenzyloxy radical. This radical decomposes to acetophenone and methyl radical. The kinetics of the reaction of ferrocyanide ion with cumene hydroperoxide indicate that the mechanism consists of the coördination of a proton with the hydroperoxy group followed by a one-electron transfer. The effect of oxygen on the reaction is discussed.

Cumene hydroperoxide may be reduced by a one-electron transfer, two successive one-electron transfers, or nucleophilic displacements.[1] The one-electron transfer process is the subject of this paper. A one-electron transfer results in the formation of the α,α-dimethylbenzyloxy radical[2,3]: $C_6H_5C(CH_3)_2O\cdot$ Kharasch[4] has obtained direct evidence for formation of this radical by its addition to an olefin.

The reduction of hydroperoxides by electron-transfer reagents is often accompanied by induced reduction caused by free radical attack on the hydroperoxide.[5] Induced reduction may be avoided by using very dilute solutions of the hydroperoxide. The ferrocyanide–cumene hydroperoxide system was found to be very suitable for studying the kinetics of reduction because of the ease with which the concentration changes of all the constituents could be followed in dilute solution.

The kinetics of the reduction of cumene hydroperoxide by ferrocyanide ion was determined by following spectrophotometrically at 430 mμ the

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[1] See the 2d paper of this series, THIS JOURNAL, **75**, 4272 (1953).

[2] J. W. L. Fordham and H. L. Williams, *ibid.*, **72**, 4465 (1950).

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

[4] M. S. Kharasch, W. Nudenberg and F. S. Arimoto, *Science*, **113**, 392 (1951).

[5] Unpublished material to be incorporated in a future paper of this series.

rate of disappearance of the ferrocyanide and following polarographically the disappearance of cumene hydroperoxide and formation of acetophenone. It was necessary to ensure the absence of oxygen. Typical curves for ferrocyanide oxidation, cumene hydroperoxide reduction and acetophenone formation are shown in Fig. 1, from which it is evident that acetophenone is formed at exactly the same rate at which the cumene hydroperoxide is reduced. This indicates that the α,α-dimethylbenzyloxy radical is not further reduced under the conditions of this experiment. It will be noticed that the amount of ferrocyanide oxidized is not quite equal to the amount of hydroperoxide reduced (*e.g.*, at 900 sec., 3.2×10^{-3} mole/liter of ferrocyanide is oxidized and 3.5×10^{-3} mole/liter of cumene hydroperoxide is reduced). This difference could be attributed to a small amount of induced reduction of the hydroperoxide, but the true explanation probably lies in a slight amount of reduction of the hydroperoxide by the mercury in the cell of the dropping mercury electrode, a phenomenon which may be observed by the formation of a film on a mercury surface when in contact with an aqueous solution of the hydroperoxide. For this reason, the ferrocyanide rate curves were used for analysis of the kinetic data.

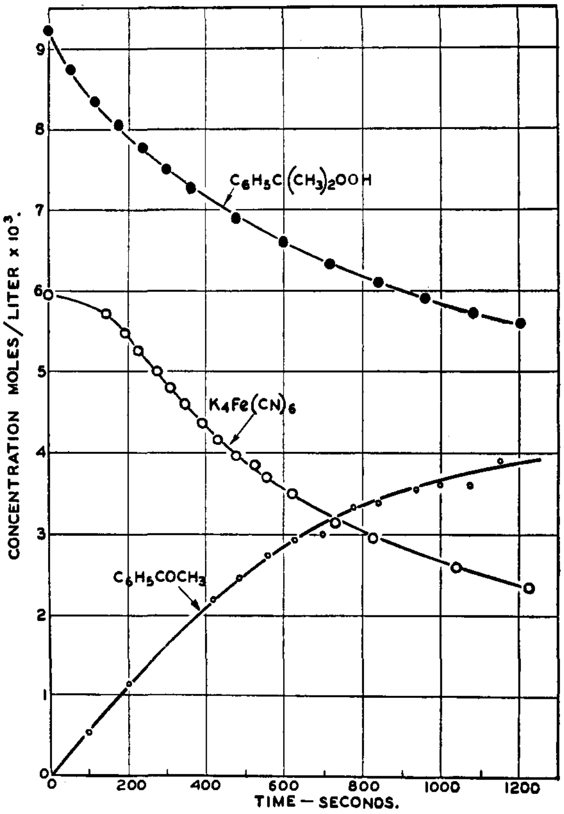

Fig. 1.—Reaction of cumene hydroperoxide and potassium ferrocyanide at 25 ± 0.1° and *p*H 9.21.

Effect of Oxygen.—The effect of dissolved oxygen on the rate of oxidation of the ferrocyanide is clearly shown in Fig. 2, from which it is evident that oxygen inhibits the rate of oxidation. Analogous experiments, performed to determine the rate of reduction of the hydroperoxide, led to the unexpected conclusion that oxygen did not simultaneously inhibit the reduction of the hydroperoxide. The presence of hydrogen peroxide (1×10^{-3} *M*) had an effect similar to oxygen in that it inhibited the ferrocyanide oxidation without inhibiting the hydroperoxide reduction. This can be explained by the known fact that hydrogen peroxide will reduce ferricyanide[6] and suggests that a similar material, capable of reducing ferricyanide, is formed during the oxygen inhibition of ferrocyanide oxidation. This oxygen inhibition is also associated with the accumulation of a material capable of rapidly oxidizing the ferrocyanide, since, as shown in Fig. 2, an accelerated oxidation of ferrocyanide takes place after a relatively long period of oxygen inhibition. Oxygen undoubtedly exerts its effect by reacting with methyl radicals which are readily oxidized to methylperoxy radicals.[7] Since the amount of ferrocyanide oxidized is equivalent to the cumene hydroperoxide reduced regardless of whether or not oxygen inhibition is present, then the accumulation of the reducible material is accompanied by an equivalent of substance capable of reducing ferricyanide as rapidly as it is formed.

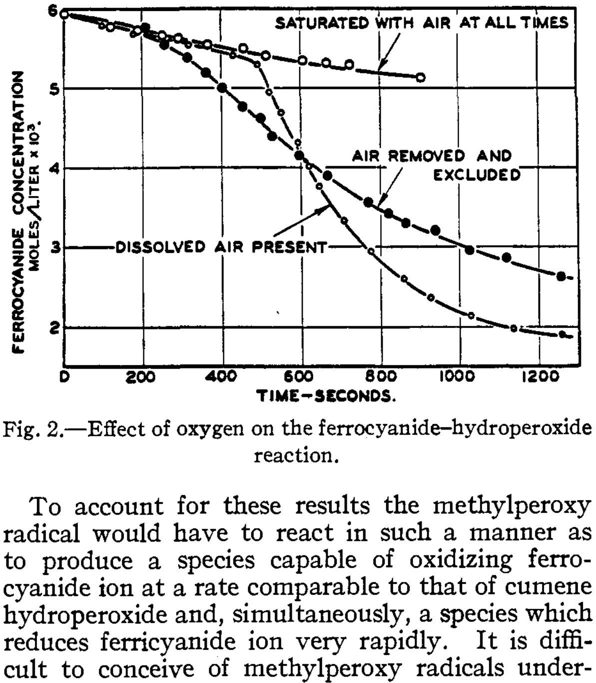

Fig. 2.—Effect of oxygen on the ferrocyanide–hydroperoxide reaction.

To account for these results the methylperoxy radical would have to react in such a manner as to produce a species capable of oxidizing ferrocyanide ion at a rate comparable to that of cumene hydroperoxide and, simultaneously, a species which reduces ferricyanide ion very rapidly. It is difficult to conceive of methylperoxy radicals undergoing disproportionation or reaction with solute to give rise to an oxidizing and reducing species. A possible solution is the reaction of methylperoxy radicals with water to produce methyl hydroperoxide (the oxidizing species) and hydroxyl radical

$$CH_3OO\cdot + H_2O \rightleftharpoons CH_3OOH + \cdot OH$$

Hydroxyl radical, under certain conditions, can act as a reducing agent.[8] The heat of reaction can be approximately calculated if it is assumed that the O–H bond dissociation energy is near that for hydrogen peroxide (102 kcal., ref. 8, p. 386); on

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[6] J. R. Partington, "Textbook of Inorganic Chemistry," 4th Ed., The Macmillan Co., New York, N. Y., 1933, p. 302.

[7] J. H. Raley, L. M. Porter, F. F. Rust and W. E. Vaughan, THIS JOURNAL, **73**, 15 (1951).

[8] N. Uri, *Chem. Revs.*, **50**, 417 (1952).

this basis, the reaction is only 7 kcal. endothermic and, therefore, could be quite feasible.

Mechanism.—The rates of ferricyanide formation at several *p*H levels and at a constant ionic strength of 0.13 are given in Fig. 3.

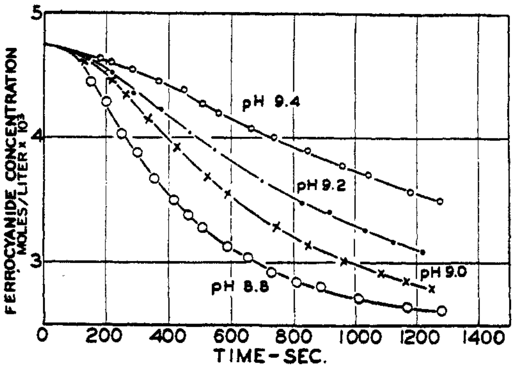

Fig. 3.—Rates of ferricyanide formation as function of *p*H: ionic strength 0.13; $(ROOH)_0 = 3.4 \times 10^{-3}\ M$.

Let P = molal concentration of hydroperoxide; Re = molal concentration of ferrocyanide. Assuming that the rate of reduction of hydroperoxide is first order with respect to each of the hydroperoxide, ferrocyanide and hydrogen-ion concentrations, then in a buffered solution

$$-\frac{dRe}{dt} = -\frac{dP}{dt} = KiPRe$$

where $Ki = Ki' \cdot (H^+)$. Integrating this equation gives

$$\log (P)_0/(Re)_0 + \log\left[\frac{(P)_0 - (Re)_0 + Re}{Re}\right] = \frac{Ki}{2.3}[(P)_0 - (Re)_0]t$$

Figure 4 gives the plot of this equation, using the data of Fig. 3. A slight induction period, probably due to traces of oxygen, is evident. A deviation from linearity in the last portion of the straight lines is noticeable at the lower *p*H levels. This deviation is caused by insufficient buffer capacity. Ki may be calculated from the slopes of the straight lines in Fig. 4, then from the values of Ki and (H^+), Ki' may be calculated. The pertinent data are shown in Table I. The constancy of Ki' agrees with the assumptions made.

TABLE I

RATE CONSTANT FOR CUMENE HYDROPEROXIDE-FERROCYANIDE REACTION AT 25°

$(H^+) \times 10^9$	Slope $\times 10^4$	Ki	$Ki' \times 10^{10}$
0.398	0.59	0.105	2.64
0.632	1.00	.178	2.82
1.00	1.41	.250	2.50
1.59	2.10	.373	2.34

At least three mechanisms are consistent with the kinetics of this oxidation–reduction reaction.

$R = C_6H_5C(CH_3)_2$ $Re = Fe(CN)_6^{----}$ $Ox = Fe(CN)_6^{---}$

$Ki = Ki'$

$$ROOH \underset{}{\overset{K}{\rightleftarrows}} RO^+ + OH^- \qquad (A)$$

$$RO^+ + Re \xrightarrow{k} RO\cdot + Ox$$

$$ROOH + H_3O^+ \overset{K}{\rightleftarrows} ROOH_2^+ + H_2O \qquad (B)$$

$$ROOH^+_2 + Re \xrightarrow{k} RO\cdot + Ox + H_2O$$

$$Re + H^+ \overset{K}{\rightleftarrows} HRe \quad K = 10^{-5} \qquad (C)$$

$$ROOH + HRe \xrightarrow{k} RO\cdot + H_2O + Ox$$

Each of these processes is followed by the decomposition of the dimethylbenzyloxy radical. For mechanism A, Ki' may be calculated by multiplying Ki by (OH^-); its value would be about 3×10^{-6}. Some idea of the plausibility of this mechanism may be gained by calculating a range of values for K. The activation energy for the reaction of the oxonium ion and ferrocyanide ion should not be very high from the nature of the reaction and from the fact that the charges on reacting species are opposite. Assuming E lies between 4 and 20 kcal./mole, $P = 1$ and $Z = 10^{13}$ liter/mole sec., then k, calculated from $k = PZe^{-E/RT}$ lies between 10^{10} and 10^{-2} liter/mole sec. The corresponding value of K, therefore, lies between 10^4 and 10^{-8} (a value of P less than one, of course, lowers the value). Attempts to measure the base dissociation constant of cumene hydroperoxide have never indicated a value of this order of magnitude. Actually, Kolthoff and Medalia[9] find that the acid dissociation constant is 2.5×10^{-13}. On the basis of this argument mechanism A may be eliminated.

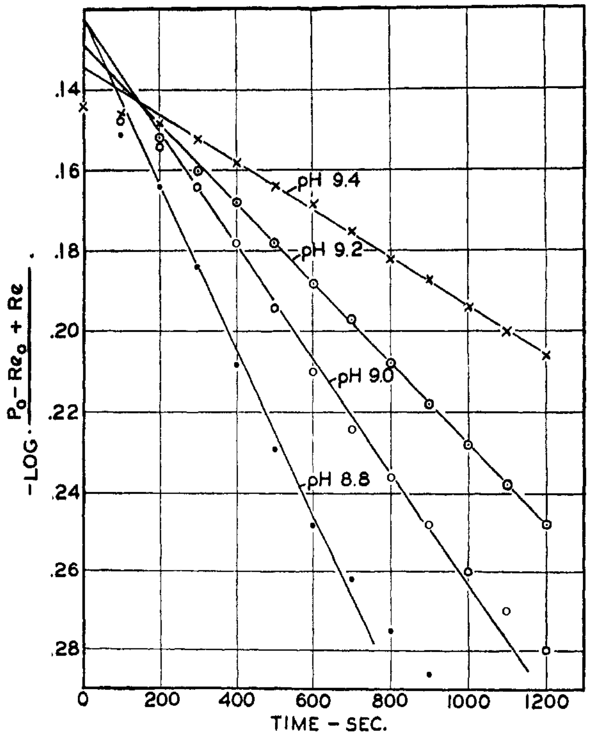

Fig. 4.—Determination of Ki: P = concentration of cumene hydroxyperoxide in moles/l.; Re = concentration of ferrocyanide in moles/l.

The value of K in mechanism C is about 1 ×

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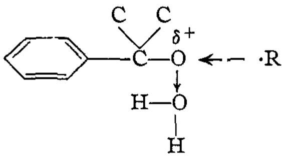
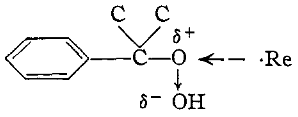
[9] I. M. Kolthoff and A. I. Medalia, THIS JOURNAL, 71, 3789 (1949).

10^{-5} at 25°[10] which gives a value of 3×10^{15} mole/liter sec. for k—a value far too high for a bimolecular reaction. Also, it is difficult to see why $HFe(CN)_6^{-3}$ should react so readily with the hydroperoxide while $Fe(CN)_6^{-4}$ does not react at all. On this basis, mechanism C is eliminated.

The above arguments leave mechanism B as the most probable one. The reason that the coordination of a proton is required can be understood from a consideration of the energetics involved. By considering the ferrocyanide ion as a nucleophilic reagent, it is obvious that transition state (a) requires less activation energy than (b) because of the separation of charge in (b)


a


b

A further question that arises is why the ferrocyanide ion is able to reduce the hydroperoxide by a one-electron transfer, whereas the iodide ion[1] preferably reduces the hydroperoxide by a slow nucleophilic attack (ionic). The necessary unpairing of a pair of electrons may be aided in the case of ferrocyanide by resonance. Thus, one of the possible resonance forms[11] of ferrocyanide may include the bond type $\mathrm{Fe{=}C{=}\ddot{N}{:}^{-}}$, and it is conceivable that, when one of the nitrogens of the outer periphery of the ferrocyanide ion is in the vicinity of the oxygen of the hydroperoxide group, an electron could transfer from the nitrogen to the oxygen. This process would be aided by the resonance stabilization of the resulting ferricyanide ion.

Experimental

Materials.—Potassium ferricyanide—Baker's C.P. material recrystallized twice from water and dried in a vacuum oven at 80°. Potassium ferrocyanide-Baker's C.P. material. Boric acid—Baker and Adamson reagent-grade material recrystallized once from water and dried at room temperature. Potassium chloride—Baker's C.P. material recrystallized from water and dried at 110°. Cumene hydroperoxide—material of 99% purity prepared by washing the sodium salt thoroughly with benzene, neutralizing with CO_2 in the presence of water, and removing volatile material from the hydroperoxide under reduced pressure.

Rate Studies.—The rate of reduction of cumene hydroperoxide and the rate of formation of acetophenone were determined continuously with the aid of the Sargent polarograph. Five ml. of a 4.55×10^{-3} M solution of cumene hydroperoxide buffered with boric acid and carbonate-free sodium hydroxide[12] (the ionic strength was kept constant by varying the potassium chloride concentration as the sodium hydroxide concentration was varied) was placed in the cell containing the dropping mercury electrode, and nitrogen was passed through for 10 minutes; then 1 ml. of a 2.84×10^{-2} M solution (previously sparged with nitrogen) of potassium ferrocyanide was introduced into the cell; the chart movement of the polarograph was started simultaneously. The rate of chart movement gives an accurate record of time. The voltage was maintained constant at 0.6 v. and the full-scale sensitivity was set to 50 μa. Inasmuch as the initial concentration of hydroperoxide and the initial wave height are known, then, if the wave height (W.H.) is proportional to the concentration of hydroperoxide throughout the whole range of reaction, the concentration at any time is given by

$$\mathrm{ROOH}_t = \mathrm{ROOH}_0 \times \frac{\mathrm{W.H.}_t}{\mathrm{W.H.}_0}$$

A previous calibration showed that this linear relationship held throughout the entire range of reaction.

The acetophenone concentration was determined in a different manner. The reaction and chart movement were started simultaneously as before, but the voltage was allowed to vary from 1.5 to 1.8 v. in order to get the complete acetophenone wave (since the base of the wave was continuously changing). This procedure was continuously repeated. A correction was applied to each measured wave height to take into account the drop in the base of the wave during the time elapsed in changing the voltage from 1.5 to 1.8.

The rate of formation of ferricyanide was determined with the aid of the Beckman spectrophotometer at 452 mμ. Beer's law is obeyed at this wave length over the range of concentration of interest in these kinetic studies, the molar extinction coefficient being 192. The cell was maintained at 25° by circulating water from a constant-temperature bath through the hollow housing containing the cell. Oxygen was excluded from the mixtures by the following procedure. A measured volume of the buffered cumene hydroperoxide solution was placed in a flask, immersed in the constant-temperature bath, and nitrogen was passed through for 15 minutes; simultaneously nitrogen was passed through the ferrocyanide solution (also kept at 25°). At zero time, a measured volume of the ferrocyanide solution was transferred to the hydroperoxide solution and the resulting mixture was transferred to the absorption cell by gas pressure in a nitrogen atmosphere. Finally, the cell was capped and transferred to the spectrophotometer for continuous measurement of optical density.

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(10) I. M. Kolthoff and W. J. Tomsicek, *J. Phys. Chem.*, **39**, 955 (1935).

(11) L. Pauling, "Nature of Chemical Bond," 2nd edition, Cornell University Press, Ithaca, N. Y., 1944, p. 255.

(12) Clark and Lubs buffer mixture, "Lange's Handbook of Chemistry," 4th Ed., Handbook Publishers, Inc., Sandusky, Ohio, 1941, p. 943.