was closely related to oxygen consumption and that similar values of the activation energy were obtained over a wide variation of reactant ratios and total pressure. Nevertheless the value of 20 kcal. per mole for the activation energy of *o*-xylene as at present obtained is about one half that of the earlier one reported. The latter, however, was based on only three runs at about 425° to 450° C.

Induction times or ignition lags may be defined in different ways which are not exactly comparable. Furthermore, they undoubtedly vary with the variety of flow and mixing patterns obtained in different reactor configurations. No ignition lag times have been reported for *o*-xylene. Salooja (*6*) reported ignition lag times for a number of aromatic and other hydrocarbons, calculated from the minimum residence time at which, for a given temperature, cool flames or "normal ignition phenomena" were observed. The reactor was of a rather complex conical shape, including an inner core, in order to maintain as near uniform temperature as possible. Using stoichiometric and fuel-rich *m*-xylene–air ratios, the lowest temperature at which he could observe an ignition was 660° C. at which the ignition lag time was 4 seconds. The insignificantly small induction period in our reactor may well be due to the use of the small glass baffle which, beside breaking up the inlet jet, provides an eddy recirculation pattern at the inlet to the reactor. Beyond that, our system is fuel-lean and our definition of induction period is different.

In gas phase reactions catalyzed by a solid there may occur interactions between homogeneous and heterogeneous kinetic paths; in particular, free radicals may be formed on the catalyst surface and released to the gas phase where they may propagate a homogeneous reaction. On the other hand the catalyst surface may cause the recombination or inactivation of radicals which otherwise might cause chain propagation in the gas phase. At present no information is available to indicate whether the homogeneous reaction will be increased or decreased in the presence of a packed bed of catalyst. If, however, we regard the two processes as occurring separately, the above results can be used to estimate the extent of homogeneous oxidation in the void space in a catalyst bed. For example, at 550° C. and 0.15-second contact time, which may represent one set of industrial conditions, we estimate that approximately 2% of *o*-xylene which disappear will have reacted homogeneously. Further losses may be expected where local hot spots occur or from reaction occurring in the hot gases leaving the catalyst bed before they can be reduced in temperature.

In laboratory units it is common practice to maintain isothermal conditions in the reactor well above and below the catalyst bed. In addition the residence time is often higher than in commercial units. For possibly typical laboratory conditions of 530° C. and residence time of 1.25 seconds, approximately 16% of the *o*-xylene entering will disappear by homogeneous gas phase reaction. These estimates indicate that probably at least under some reaction conditions in laboratory and plant a portion of the so-called catalytic reaction is instead homogeneous in nature.

Acknowledgment

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OXIDATION OF ACETALDEHYDE TO ACETIC ANHYDRIDE

BENJAMIN H. CARPENTER,[1] *Graduate Center, West Virginia University, Charleston, W. Va.*

A kinetic model, useful for reactor design, is developed for the catalytic oxidation of acetaldehyde to acetic anhydride in the presence of an organic ester diluent. The model is based upon a mechanism involving a sequence of seven reactions established by previous investigations or by this study. Data obtained with tank flow reactors at 56° C. offer new evidence that acetaldehyde monoperacetate is formed as an intermediate which is decomposed, in the presence of cobalt and copper acetate, to form acetic anhydride and water. Acetic anhydride is thus shown to be a precursor of acetic acid rather than a parallel product in the decomposition of acetaldehyde monoperacetate. Acetic acid is produced by subsequent hydrolysis of the anhydride. Estimates of the rate constants involved in the model are presented, together with their standard errors.

ACETIC anhydride is produced, together with acetic acid, by reaction of liquid acetaldehyde with dissolved oxygen in the presence of metal ions. By conducting the reaction in the presence of an inert diluent, the yield of acetic anhydride is substantially increased (*3*). A mechanism for this reaction was proposed by Heatley (*5*). The mechanism indicated that peracetic acid was formed initially, and subsequently combined with acetaldehyde to give both acetic anhydride and acetic acid directly. Differential equations based on the suggested mechanism were developed and solved by making certain assumptions concerning limiting values of the specific reaction rates. The results indicated that some important side reactions must be included to account for observed concentrations of acetic anhydride.

Subsequent investigations (*6, 8*) disclosed the formation of a complex, acetaldehyde monoperacetate, by reaction of per-

[1] Present address, Research and Development Department, Chemicals Division, Union Carbide Corp., South Charleston, W. Va.

acetic acid and acetaldehyde prior to the generation of either the anhydride or the acid.

In this study, a new mechanism is developed which includes the complex as an intermediate, and which leads to a kinetic "model," useful as a basis for reactor design. Data obtained from differential reactors operated at steady state disclose that the catalytic decomposition of the complex yields acetic anhydride initially in an ester solvent, and that the acetic anhydride is the precursor of acetic acid, which is formed by subsequent hydrolysis. Specific reaction rates are estimated.

Development of a Reaction Mechanism

When exposed to oxygen or air, acetaldehyde is slowly oxidized to peracetic acid, which in turn further reacts with the aldehyde. The rate of oxidation is increased by light, and by cobalt, copper, and manganese acetates. Bawn, Hobin, and Raphael (*1*) found that the oxidation with each of these metal acetates followed a similar course when conducted in glacial acetic acid. The course conforms to the general kinetic relationship.

$$\frac{dO_2}{dt} = k\ (\text{acetaldehyde})^{1.5}\ (\text{catalyst})^{0.5} \qquad (1)$$

Their analysis of the products showed that the reaction proceeds in two stages.

The aldehyde is oxidized to peracetic acid.
The peracetic acid reacts with acetaldehyde to give acetaldehyde monoperacetate.

The reaction leading to peracetic acid is apparently initiated by an electron transfer between the acetaldehyde and the higher valence state of the metal ion.

$$M^{3+} + CH_3CHO \rightarrow M^{2+} + CH_3CO. + H^+ \qquad (2)$$

This reaction initiates the following chain process.

$$CH_3CO. + O_2 \rightarrow CH_3COOO. \qquad (3)$$

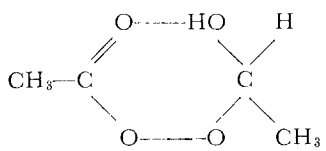
$$CH_3COOO. + CH_3CHO \rightarrow CH_3COOOH + CH_3CO. \qquad (4)$$

The metal ion is maintained in the higher valence state by the reaction cycle:

$$CH_3COOOH + M^{2+} \rightarrow CH_3COO. + M^{3+} + OH^- \qquad (5)$$

$$CH_3COOOH + M^{3+} \rightarrow CH_3COOO. + M^{2+} + H^+ \qquad (6)$$

The peracetic acid thus formed reacts with acetaldehyde to form a complex which was first isolated by Kagan and Lubarsky (*6*) and found to be stable at $-30°$ C. On the basis of infrared spectra, Starcher, Phillips, and Frostick (*10*) established for this complex the ring structure, acetaldehyde monoperacetate.



For simplicity of notation, it is designated throughout this paper as AMP. This complex decomposes readily to acetic acid upon heating or on treatment with manganese acetate catalyst.

$$CHCO_3H + CH_3CHO \rightleftarrows AMP \quad E_A = 7 \text{ kcal./mole} \qquad (7)$$

$$AMP \rightarrow 2CH_3COOH \quad E_A = 15 \text{ to } 16 \text{ kcal./mole} \qquad (8)$$

Kagan and Lubarsky (*6*) give these and other activation energies for many of the elementary processes involved in the mechanism of aldehyde oxidation. Since constants in the Arrhenius equations for elementary processes are just beginning to be evaluated, the assessment of activation energies is not easy, and values given are approximate.

The decomposition of AMP is accelerated by metal ions and by water (*6*). In fact, the rate is a function of the ion concentration. Decomposition of AMP shifts the equilibrium in Equation 7 to the right, so that the rate of formation of AMP is determined by its rate of decomposition and is varied by varying the catalyst or the water content of the reaction mixture.

In the presence of inert diluents, the decomposition of AMP yields both acetic anhydride and water, in addition to acetic acid. The water formed, of course, hydrolyzes the anhydride to acetic acid. Plyler and Barr (*9*) found that the specific reaction rate for this hydrolysis increased as the aldehyde content of the reaction decreased.

As established by Heatley (*5*), the reaction between acetic anhydride and peracetic acid to form diacetyl peroxide is a necessary part of the over-all mechanism.

$$(CH_3CO)_2O + CH_3COOOH \rightarrow (CH_3CO)_2O_2 + CH_3COOH \qquad (9)$$

The diacetyl peroxide produced reacts with water to regenerate peracetic acid.

$$(CH_3CO)_2O_2 + H_2O \rightarrow CH_3COOOH + CH_3COOH \qquad (10)$$

These investigations imply that to delineate the mechanism whereby acetaldehyde is catalytically oxidized in an inert solvent to acetic anhydride and acetic acid, seven reactions must be considered. Two reactions occur in which acetaldehyde is directly involved: the addition of dissolved oxygen to form peracetic acid and the reaction between peracetic acid and acetaldehyde to give AMP. The decomposition of AMP must be apportioned between acetic anhydride and acetic acid. In fact, control of the ratio of these products is of primary importance in any commercial use of this process. The acetic anhydride, once formed, is hydrolyzed to some extent by the water that is formed concurrently, and some of it will react with peracetic acid to form diacetyl peroxide. Diacetyl peroxide reacts with water to regenerate peracetic acid.

Consistent with the behavior of these components as previously and herein demonstrated, the following mechanism is proposed.

$$CH_3CHO + O_2 \rightarrow CH_3COOOH \qquad (11)$$

$$\text{Rate} \cong k_1 V\ [CH_3CHO]^{1.5}\ [\text{catalyst}]^{0.5}$$

$$CH_3COOOH + CH_3CHO \rightleftarrows AMP \qquad (12)$$

$$\text{Rate} \cong k_2 V\ [CH_3COOOH]\ [CH_3CHO]$$

where k_2 is the net specific reaction rate.

$$AMP \rightarrow (CH_3CO)_2O + H_2O \qquad (13)$$

$$\text{Rate} \cong k_3 l_4 V\ [AMP]$$

where l_4 is the fraction of [AMP] which goes directly to acetic anhydride and water.

$$AMP \rightarrow 2\ CH_3COOH \qquad (14)$$

$$\text{Rate} \cong k_3\ (1 - l_4) V\ [AMP]$$

$$(CH_3CO)_2O + H_2O \rightarrow 2\ CH_3COOH \qquad (15)$$

$$\text{Rate} \cong k_5 \left(1 + \frac{l_6}{[CH_3CHO]}\right) [(CH_3CO)_2O]$$

$$(CH_3CO)_2O + CH_3COOOH \rightarrow (CH_3CO)_2O_2 + CH_3COOH \qquad (16)$$

$$\text{Rate} \cong k_7 V\ [(CH_3CO)_2O]\ [CH_3COOOH]$$

$$(CH_3CO)_2O_2 + H_2O \rightarrow CH_3COOOH + CH_3COOH \qquad (17)$$

$$\text{Rate} \cong k_8 V\ [(CH_3CO)_2O_2]\ [H_2O]$$

The following simplified notation will facilitate the development of the rate equations involved in this mechanism.

a = $[CH_3CHO]$ = acetaldehyde, moles/liter
b = $[(CH_3CO)_2O]$ = acetic anhydride, moles/liter
c = $[CH_3COOH]$ = acetic acid, moles/liter
e = $[CH_3COOOH]$ = peracetic acid, moles/liter
f = [AMP] = acetaldehyde monoperacetate, moles/liter
g = $[(CH_3CO)_2O_2]$ = diacetyl peroxide, moles/liter
h = $[H_2O]$ = water, moles/liter

The condition considered in deriving reaction rates is the absorption of oxygen from air into a liquid system at a uniform rate which, owing to the instantaneous reaction, determines the rate of formation of peracetic acid (k_1 gram moles per liter of reactor volume per hour). The rates of production of the various susbstances then follow Equations 18 to 24, derived from Equations 11 to 17.

Acetaldehyde

$$\frac{da}{dt} = -k_1 - k_2ae \tag{18}$$

Acetic anhydride

$$\frac{db}{dt} = k_3l_4f - k_5\left(1 + \frac{l_6}{a}\right)b - k_7be \tag{19}$$

Acetic acid

$$\frac{dc}{dt} = 2k_3(1 - l_4)f + 2k_5\left(1 + \frac{l_6}{a}\right)b + k_7be + k_8gh \tag{20}$$

Peracetic acid

$$\frac{de}{dt} = k_1 - k_2ae - k_7be + k_8gh \tag{21}$$

Acetaldehyde monoperacetate

$$\frac{df}{dt} = k_2ae - k_3f \tag{22}$$

Diacetyl peroxide

$$\frac{dg}{dt} = k_7be - k_8gh \tag{23}$$

Water

$$\frac{dh}{dt} = k_3l_4f - k_5\left(1 + \frac{l_6}{a}\right)b - k_8gh \tag{24}$$

Evaluation of Specific Reaction Rates

The procedure for evaluation of the constants was formulated under the following assumptions: k_1 is set equal to the rate of transfer of oxygen to the liquid phase.

Assuming steady state with respect to the peroxides, the peracetic acid concentration does not change with time, and $de/dt = 0$, from which $k_1 + k_8gh = k_2ae + k_7be$. Similarly, acetaldehyde monoperacetate does not change with time, and

$$\frac{df}{dt} = 0, \text{ from which } k_2ae = k_3f$$

Diacetyl peroxide does not change with time, and

$$\frac{dg}{dt} = 0, \text{ from which } k_7be = k_8gh$$

Under these conditions, $k_1 = k_2ae$ and $-da/dt = +k_1 + k_2ae = 2k_2ae$, from which $k_2 = \frac{-da}{dt}\frac{1}{2ae}$. Also, $f = \frac{k_2ae}{k_3}$. Using $e = \frac{k_1}{k_2a}$ gives $f = k_1/k_3$, so that $k_3 = k_1/f$.

Under these assumptions, experimental data obtained from two different reactant mixes will suffice to provide estimates of the rate constants, since the hydrolysis constants, k_5 and l_6, can be determined by direct measurement of the rate of depletion of acetic anhydride in the reaction medium. The constant k_7 is most precisely determined by the acetic anhydride equation, utilizing estimates of k_5 and l_6, and eliminating l_4 from the two equations for two different experiments. This procedure then permits separate evaluation of l_4 for each experiment. l_4 is the constant proportioning AMP between acetic anhydride and acetic acid. It will be shown to be essentially equal to unity.

Experimental

Experimental work falls into three phases: establishing the ability to distinguish the three peroxides; determining the rate of hydrolysis of acetic anhydride in the reaction medium; and determining the rates of formation of the products pertinent to the mechanism.

Stirred Tank Reactions. The reaction system is shown schematically in Figure 1. The liquid components of the reaction mixture were fed to an agitated reactor into which air was sparged to supply oxygen.

Samples of reactor feed and product streams were taken simultaneously, chilled at once in a dry ice–acetone mixture to prevent further reaction, and then subjected almost immediately to complete analysis. Prior to sampling, the process was brought to steady state at 56° C. All flow rates were metered.

Exhausted air was withdrawn, first through a scrubber where contained vapors were absorbed in acetic acid and isopropyl acetate, and then through a water scrubber. The acetic acid and isopropyl acetate were then fed to the reactor, while the water effluent was sewered. Cobalt-copper catalyst solution was prepared using a mixed acetic acid–acetic anhydride solvent.

Analysis. Reactor feed and make samples were analyzed chemically for the following major components: acetaldehyde, acetaldehyde monoperacetate, acetic acid, acetic anhydride, diacetyl peroxide, peracetic acid, and water. Minor components, measured by mass spectrometer, were ethanol, acetone, carbon dioxide, and methane. These components were utilized in material balance calculations, but were not considered as involved in the mechanism for the main products. They probably arise in vapor-phase side reactions.

Bawn and Williamson (*2*) found that peracetic acid could be

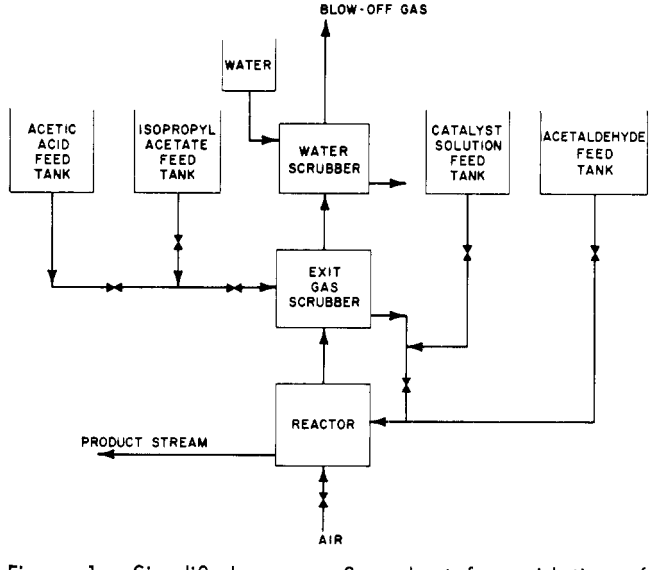


Figure 1. Simplified process flow sheet for oxidation of acetaldehyde

determined by titration of the iodine liberated from potassium iodide in 1N aqueous sulfuric acid. In this medium, AMP is decomposed at once to acetic acid. Diacetyl peroxide would react slowly, if at all. Since these investigators were not concerned with the separate estimation of diacetyl peroxide, they obtained a total peroxide using a glacial acetic acid solution of the sample to which powdered potassium iodide was added. By avoiding contact with mineral acids, AMP was preserved to react with the iodide. The decomposition of AMP to acetic acid appears to be dependent upon the presence of the cobalt and copper salts. Starcher (*10*) employed potassium iodide in sulfuric acid to determine peracetic acid plus AMP in metal-free samples. Without the metal salts, AMP reverts to peracetic acid.

Inasmuch as the present study required estimation of diacetyl peroxide, the following three test methods were developed by further investigation.

METHOD A, PERACETIC ACID. Peracetic acid alone was determined by introducing a 5-ml. sample into aqueous 1N sulfuric acid, whereupon AMP was decomposed and the peracetic acid reacted with 1 gram of solid potassium iodide. The liberated iodine was titrated immediately with 0.01N sodium thiosulfate to the first colorless end point.

METHOD B, DIACETYL PEROXIDE. Both peracetic acid and diacetyl peroxide were determined by introducing a 5-ml. sample into 10 ml. of 4N sulfuric acid, 15 ml. of 10% potassium iodide, and 4 or 5 drops of ammonium molybdate solution. The mixture was allowed to stand 15 minutes, diluted with 100 ml. of distilled water, and titrated with 0.01N sodium thiosulfate solution to a starch end point. No color should reappear after shaking 15 seconds once the first end point is reached.

METHOD C, ACETALDEHYDE MONOPERACETATE. In both previous methods, AMP is decomposed by the mineral acid. To determine total peroxide, including AMP, a 5-ml. sample was added to 50 ml. of glacial acetic acid to which 5 ml. of acetic anhydride had previously been added. Three grams of solid potassium iodide were added, and the mixture was let stand in the dark for 15 minutes. The liberated iodine was titrated with 0.01N sodium thiosulfate to a colorless end point. Blanks were run on all reagents in each of these methods.

The experiments employed both cobalt and copper catalysts. Cobalt does not interfere in the peroxide determinations. Copper does interfere. A correction equal to two equivalents of potassium iodide per atom of copper is required. Copper was determined by a photometric method.

Twenty samples were tested by these methods to determine their precision and ability to distinguish the peroxides. The results, shown in Table I, as equivalent weight per cent peracetic acid, support the conclusion that the three peroxides can be separately estimated. Additional test methods were as follows.

ACETIC ANHYDRIDE, ACETIC ACID, AND ISOPROPYL ACETATE. A 3-ml. sample was introduced into 50 ml. of anhydrous methanol and titrated with 0.5N sodium methylate in pyridine to a phenolphthalein end point. This titration gave the acetic acid plus the acetic anhydride. Another 3-ml. sample was added to 50 ml. of water and let stand for 20 minutes to hydrolyze the anhydride. The solution was cooled to 10° C. and then titrated with 0.5N aqueous sodium hydroxide to a phenolphthalein end point. This measured the acetic acid plus twice the acetic anhydride. The amount of acetic anhydride and the amount of acetic acid were obtained from these two titrations. The ester in the sample was stabilized by keeping the solution cold.

After titration with aqueous sodium hydroxide, a 40-ml. excess of this reagent was added, and the solution was heated to near boiling, cooled, and back-titrated to measure the ester content.

WATER. Water was determined by titrating a 1- to 5-ml. sample with Karl Fischer's reagent.

Simultaneous liquid and vapor samples were analyzed for minor by-products by means of a mass spectrometer. Acetone, carbon dioxide, ethyl acetate, ethyl ether, ethyl formate, formic acid, methyl acetate, methane, and methanol were determined in this manner. These components were not considered in delineating the mechanism for the main products of liquid-phase reaction, but were measured for possible future study of side reactions, and to aid the establishment of material balances for the experiments.

Rate of Hydrolysis. Data showing the rate of hydrolysis of the acetic anhydride were obtained using reactor samples in order to take into account the possible effects of the metal ions. Samples were charged to pressure bottles to prevent loss of acetaldehyde and placed in a constant temperature bath at 56° ± 0.1° C. The heated contents were agitated to maintain uniform temperature and composition. Samples were withdrawn periodically to determine the remaining acetic anhydride and water. The data, shown in Figure 2, were used to determine $k_5 = 0.048$ hr.$^{-1}$ and $l_6 = 12.55$ (l_6 accounts for the effect of acetaldehyde concentration on the rate of hydrolysis).

Results and Data Analysis

Table II shows the reaction mix composition and the production rates for two experiments. The total active metals amounted to 0.013 mole per liter for experiment A, and 0.015 mole per liter for experiment B.

Concentrations shown in the table were computed directly from analyses of the reactor samples. Productivities were obtained through material balances involving flow measurements into and out of the reactor. While the analytical tests could be conducted under precise control, and were judged as accurate except for random error, the flowmeters were subject to small environmental effects sufficiently different from calibration conditions to cause a slight imbalance. Therefore prior to the calculation of productivities, the flow measurements were adjusted statistically, each adjustment being weighted in inverse proportion to the square of its standard deviation. This method of adjustment, fully described by Deming (*4*), is as follows.

Minimize Σ (weighted adjustments to flows)$^2 = \Sigma(V)^2$, subject

Table I. Data Showing Presence of Three Peroxides in Reaction Mixture

		Peroxide Content Calculated as Peracetic Acid, Wt. %		
Run	*Sample*[a]	*Method A*	*Method B*	*Method C*
1	AM	0.112	0.261	0.329
	PM	0.170	0.247	0.335
2	AM	0.118	0.261	0.331
	PM	0.108	0.232	0.327
3	AM	0.123	0.219	0.347
	PM	0.086	0.191	0.263
4	AM	0.099	0.235	0.330
	PM	0.0892	0.238	0.288
5	AM	0.112	0.255	0.344
	PM	0.087	0.270	0.339
6	AM	0.154	0.376	0.440
	PM	0.248	0.334	0.675
7	AM	0.117	0.321	0.479
	PM	0.142	0.319	0.447
8	AM	0.147	0.325	0.444
	PM	0.113	0.288	0.347
9	AM	0.150	0.325	0.412
	PM	0.125	0.341	0.363
10	AM	0.201	0.377	0.457
	PM	0.191	0.346	0.408

[a] *Runs 1–5 taken from reaction mixes in which concentration of aldehyde was approximately 2 moles/liter; runs 6–10 represent aldehyde concentration of 1.5 moles/liter.*

Table II. Composition of Reaction Mix and Production Rates

Component	Concn., G. Moles/Liter			Production Rates, G. Moles/Liter, Hr.		
	Run A	Run B	Std. Dev.	Run A	Run B	Std. Dev.
Acetic anhydride	1.377	1.812	0.014	5.084	3.138	0.175
Acetic acid	6.116	4.905	0.016	4.647	2.585	1.0
Peracetic acid	0.0115	0.0024	0.00026	0.0527	−0.0165	0.016
Acetaldehyde monoperacetate	0.0120	0.0065	0.0022	0.0298	−0.0892	0.014
Diacetyl peroxide	0.0273	0.039	0.0051	0.0916	0.117	0.031
Water	1.237	1.504	0.027			
Solvent	3.440	3.300				
Acetaldehyde	1.988	1.631	0.022	15.11[a]	8.90[a]	
Oxygen				7.63[a]	4.54[a]	

[a] *Quantities consumed in formation of products involved in reaction mechanism.*

to the material balance restriction, $M = \Sigma$ (acetaldehyde input − acetaldehyde and equivalents output) = 0

PROCEDURE. Form the functions

$$f = \Sigma \text{ (weighted adjustments, } V_i) \ \delta \ V_i$$

and

$$F = f + \lambda M$$

and determine the value of λ and the values of the adjustments from equation M and the equations

$$\frac{\partial F}{\partial \text{ (flow rate } j)} = 0 \quad j = 1, 2, \ldots, 4$$

Deming shows that $\lambda = F_o/L$, where F_o = the initial value of the material balance, M, and $L = \Sigma F_j^2/w_j$. Here $F_j = \partial F_o/\partial x_j$ for flow rate x_j, and w_j = the weight assigned to flow rate x_j. Having thus computed λ, the adjustments, V_j, to be substracted from the flow measurements are

$$V_j = \frac{1}{w_j} \lambda F_j$$

Values for k_2, k_3, l_4, k_7, and k_8 were obtained by substituting the data from Table II into Equations 18 to 24, and solving algebraically, using $d/dt = \Delta/\Delta t$. Since k_1 was set equal to the rate of oxygen absorption into the well stirred liquid, and k_5 and l_6 were obtained by direct measurement of the rate of anhydride hydrolysis, this completed the fitting of the model to the data. The complete set of constants is shown in Table III.

Precision of Rate Constants. Although the limited amount of data provide limited information on the precision of the specific reaction rates, some worthwhile indications of the precision may nevertheless be obtained. The constants are derived from concentration and flow measurements, the standard deviations of which were fairly well established experimentally (Table II). Each constant was estimated using one or more of Equations 18 to 24. To obtain the error of estimate, the equation was differentiated with respect to each measurement, and these partial derivatives entered into the following error equation (*4*).

$$\text{Standard deviation, } k_i = [\Sigma \ (\partial g_i/\partial x_i)^2 \ (\text{std. dev. } x_i)^2]^{1/2}$$

where g_i = function for calculation of k_i
x_i = a measurement contained in function, g_i
std. dev. x_i = standard deviation of measurement x_i

Essentially, the standard deviation of a rate constant is expressed by a truncated Taylor series expansion, assuming the errors in the test measurements and flow measurements to be independent.

Table III. Specific Reaction Rates at 56° C.

Specific Rate	Units	Value, Run A	Value, Run B	Std. Dev.
k_1	G. moles/liter, hr.	7.63	4.53	0.56
k_2	l/g. mole, hr.	331	1138	13
k_3	Hr.$^{-1}$	636	697	63
l_4		0.97	0.97	0.2
k_5	Hr.$^{-1}$	0.048	0.048	0.005
l_6		12.55	12.55	2
k_7	l/g. mole, hr.	114.4	114.4	42
k_8	l/g. mole, hr.	53.3	8.4	22

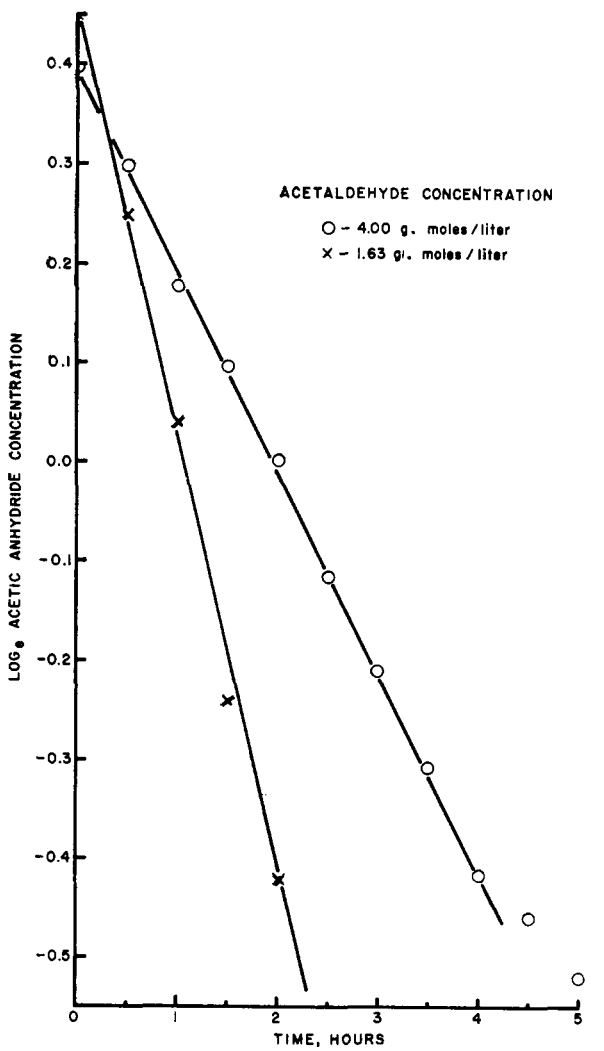


Figure 2. Effect of aldehyde concentration on rate of hydrolysis of acetic anhydride

EXAMPLE. From Equation 18

$$k_2 = \frac{4.7 \times 10^{-6} [x_1 a_1 - x_2 a_2]}{a_2 e}$$

where x_1, x_2 are flow rates into and out of the reactor, respectively, a_1, a_2 are the acetaldehyde concentrations in the streams, and e is the peracetic acid concentration in the reactor.

From this, the standard deviation of k_2 is:

$$\text{std. dev. } k_2 = \left[\left(\frac{\partial k_2}{\partial x_1}\right)^2 (\text{std. dev. } x_1)^2 + \left(\frac{\partial k_2}{\partial x_2}\right)^2 (\text{std. dev. } x_2)^2 + \left(\frac{\partial k_2}{\partial a_1}\right)^2 (\text{std. dev. } a)^2 + \left(\frac{\partial k_2}{\partial a_2}\right)^2 (\text{std. dev. } a)^2 + \left(\frac{\partial k_2}{\partial e}\right)^2 (\text{std. dev. } e)^2\right]^{1/2} = 13$$

Discussion

The results indicate that acetaldehyde monoperacetate, formed from peracetic acid and acetaldehyde, decomposes almost quantitatively to acetic anhydride and water. The proportion of this peroxide decomposing directly to the anhydride was estimated at 0.97. It is reasonable to assume that acetaldehyde monoperacetate yields acetic anhydride exclusively in an ester solvent, and that the acid is formed solely by hydrolysis of the anhydride. The mechanism can then be simplified to give

$$\frac{\Delta[\text{acetic anhydride}]}{\Delta t} = k_3 [\text{AMP}] - k_5\left(1 + \frac{l_6}{[\text{acetaldehyde}]}\right)[\text{acetic anhydride}] - k_7 [\text{acetic anhydride}] [\text{peracetic acid}]$$

and

$$\frac{\Delta[\text{acetic acid}]}{\Delta t} = 2k_5\left(1 + \frac{l_6}{[\text{acetaldehyde}]}\right)[\text{acetic anhydride}] + k_7 [\text{acetic anhydride}] [\text{peracetic acid}] + k_8 [\text{diacetyl peroxide}] [\text{water}]$$

The substantial variation in the specific rate k_2 cannot all be explained by experimental error. Although the metals concentration was controlled at ± 0.0004 mole per liter during the steady-state experiments, the observed difference in metals concentration between the two experiments was 0.002 ± 0.0006 mole per liter. Since the absorption of oxygen is proportional to the square root of the metal ion concentration (*1*), the difference in k_2 values is in part due to the difference in metal ion concentration. This suggests that values of k_2 can be controlled by controlling the concentration of catalyst.

The concentrations of peracetic acid, AMP, and acetaldehyde differ somewhat from values predicted from a calculated equilibrium constant. Bawn and Williamson (*2*) give 0.77 ± 0.14 for this constant at $10° \pm 2°$ C. Bawn, Hobin, and Raphael (*1*) give 0.36 ± 0.03 for the constant at 25° C. Extrapolating to 56° C. gives

$$K = \frac{(\text{acetaldehyde}) (\text{peracetic acid})}{(\text{AMP})} = 0.089$$

The value 0.089 has a standard deviation of 0.34. Data presented herein show $K = 1.91$ for run A and 0.61 for run B. The difference between these values, 1.3, is not statistically significant when compared with an estimated standard deviation for each of 0.54. Their average, 1.26, does differ significantly from the estimated $K = 0.089$. Either the steady-state concentrations attained in these reactions do not correspond with equilibrium concentrations, or the equilibrium was altered in the brief time required to freeze the samples and thaw them for analysis. If so, then the "model" is valid only when concentrations of peroxides are determined at 20° C.

Conclusions

The kinetic constants obtained in this study, based upon experiments, are believed to be more accurate than previous values obtained in limited solutions of the rate equations in less complete kinetic models, and will serve as sound starting values for further correlations, using numerical methods, aimed at fitting the kinetic equations to additional data. The model presented provides a basis for reactor design aimed at control of the main product ratio.

Although activation energies are reported in the literature for most of the reactions involved, study of the reactions at other temperatures is needed to determine to what extent the rate of hydrolysis of the anhydride may be decreased while maintaining the catalyzed intermediate reactions at satisfactorily high rates.

Some statistically designed experiments to elucidate the separate catalytic effects of catalyst concentration and water concentration would permit better prediction of the performance of reactors in series.

Nomenclature

In the development of a mechanism for the catalytic oxidation of acetaldehyde, the following signs and symbols are employed. More complete explanations are given in the text whenever required.

a	= acetaldehyde concentration, gram moles per liter
b	= acetic anhydride concentration, gram moles per liter
c	= acetic acid concentration, gram moles per liter
$CH_3CO.$	= free radical
e	= peracetic acid concentration, gram moles per liter
E_A	= energy of activation
f	= acetaldehyde monoperacetate concentration, gram moles per liter
F	= data adjustment function
g	= diacetyl peroxide concentration, gram moles per liter
h	= water concentration, gram moles per liter
K	= equilibrium constant
k_i	= specific reaction rate, $i \neq 4$ or 6
l_4, l_6	= modifying constants
M	= metal ion
t	= time, hours
λ	= Lag range multiplier
w	= weight assigned to flow rate
x	= flow rate
V	= volume of reaction mixture, liters
AMP	= intermediate peroxide formed from peracetic acid
$[CH_3CHO]$	= acetaldehyde, gram moles per liter
$\cong$	= equivalent to

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CARBON DISULFIDE PRODUCTION BY REACTION OF ELEMENTAL SULFUR WITH CARBONIZED LIGNITE AND WOOD CHARCOAL

EVERETT A. SONDREAL

Grand Forks Lignite Research Laboratory, Bureau of Mines, U. S. Department of the Interior, Grand Forks, N. D.

Carbon disulfide was produced at about the same high rates, using either lignite chars or wood charcoal. A maximum space velocity of 9280 hr.$^{-1}$ was achieved by reaction of sulfur and lignite char at 792° C. Raising the carbonization temperature of chars in nitrogen increased the threshold for reaction with sulfur by as much as 300° C. The activation energy for subsequently reacting chars with sulfur averaged 44,000 cal. per gram mole. Rates were first order with respect to the partial pressure of sulfur, were lowered by increasing the rate of sulfur admission, and were essentially unaffected by char size. High rates of production in a lignite-based process could offer advantages in the manufacture of carbon disulfide, if yields were attractive. Determining optimum yields will be a major objective in a forthcoming pilot plant program.

CARBON DISULFIDE ranked 49th in value among major organic chemicals in 1959, when production of 563,000,000 pounds was valued at $28,200,000 (*7*). The production of carbon disulfide is closely tied to the manufacture of regenerated cellulose (rayon and cellophane), which accounts for an estimated 72 to 80% of United States consumption. Other uses are in the manufacture of carbon tetrachloride, rubber accelerators, and insecticides.

The traditional method for the manufacture of carbon disulfide has been to make wood charcoal and sulfur react at approximately 850° C. in externally heated retorts or electric furnaces (*3*). Production of carbon disulfide from sulfur and methane has rapidly supplanted the charcoal process and was estimated to account for 40% of United States production by 1958 (*4*). Perhaps 75% of the active capacity now employs the new process (*1*, *2*).

The high price of wood charcoal and the relatively high temperature required for reaction are disadvantages of the charcoal process. This process would be more attractive if a cheaper carbon could be made to react at lower temperatures, but unfortunately substitutes for charcoal have generally proved unsatisfactory because of slow reaction rates. For example, coke requires reaction temperatures hundreds of degrees higher than those used for wood charcoal to produce carbon disulfide at even lower rates.

Carbonized lignite has proved provisionally acceptable as a substitute for charcoal. Laboratory experiments carried out in England have shown that sulfur reacts with chars made from low-rank coal at rates comparable to those with wood charcoal (*4*). In both East and West Germany, shortage of wood charcoal has forced development to the point where chars made from brown coal are being used commercially (*5*).

The work done in Europe on the use of low-rank coal for the production of carbon disulfide appears to be of special importance to the lignite-producing areas in the United States. Sulfur from natural gas has recently become available in the North Dakota lignite area, and the proximity of these raw materials could represent an opportunity for production of carbon disulfide. Potential markets within a reasonable distance could include cellophane plants in Clinton, Iowa, and Tecumseh, Kan.

North Dakota lignite is considered to be a reactive fuel, causing one to expect that it would react readily with sulfur. To substantiate this, a program of research was instituted by the Federal Bureau of Mines to determine rates of reaction between sulfur and carbonized lignite under various conditions suitable for manufacturing carbon disulfide.

Experimental Procedure

Superheated sulfur vapor in nitrogen at 1 atm. was passed through a fixed bed of char. Approximately 80 cc. of lignite char or 218 cc. of wood charcoal (50 grams of either at specified condition) was contained in a $2^1/_2$-inch i.d. stainless steel reactor which was inserted in a muffle furnace. Liquid sulfur was metered into a vaporizer (by displacement with a controlled flow of mineral oil) and nitrogen was added to obtain the desired partial pressure of sulfur. The sulfur and nitrogen were heated in a preheater to approximately 700° C. before being introduced into the reactor, so that the heat required to dissociate S_6 and S_8 to S_2 would not be absorbed in the reaction zone. After reaction, products were separated from unreacted sulfur by condensing the sulfur at 140° C. and filtering the cooled gases to remove sublimed sulfur dust. Water was removed by calcium chloride, after which the carbon disulfide was separated in a condenser cooled with sublimed carbon dioxide. Gas leaving the condenser contained nitrogen, hydrogen sulfide, and carbonyl sulfide.

Figure 1 is a schematic drawing of the apparatus.

Chars Used in Experiments

Lignite chars were prepared in the laboratory by heating raw lignite in a nitrogen atmosphere to a predetermined temperature and holding at that temperature for 1 to 2 hours. For some runs, the effective maximum carbonization tempera-