Kinetics of the Reaction Between Chlorine and Oleic Acid in Carbon Tetrachloride Solution[1]

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ABSTRACT

Kinetic data have been obtained for the reaction between chlorine and oleic acid in carbon tetrachloride solution by measuring the chlorine depletion and hydrogen chloride production as a function of residence time in a rod-like flow system. The data are well correlated by a kinetic model incorporating parallel, second-order addition and substitution reactions. Measured reaction rates are an order of magnitude less than those reported in a previous investigation which neglected substitution reactions.

INTRODUCTION

It appears that the only previous study of the kinetics of this system is due to Roper (1), who employed a continuous flow technique with a tubular reactor. Chlorine concentrations were determined by passing the partially reacted mixture through a 5N hydrochloric acid solution until equilibrium partition of chlorine was established between the two phases. Since the distribution coefficient had been measured previously, analysis for chlorine in the hydrochloric acid phase could be used to infer the concentration of chlorine in the reactor outlet stream. It was assumed that the only significant reaction was addition of chlorine across the double bond of the oleic acid $C_8H_{17}CH/CH\ (CH_2)_7CO_2H$, and data were fitted to a second-order rate expression. The reported value of the reaction rate constant was 159 liter/gmole sec at 22 C, and 192 liter/gmole sec at 41 C, yielding a value of 2000 cal/gmole for the activation energy. These experiments were all conducted in the dark.

Now Roper's assumption that the reaction is exclusively one of chlorine addition is contrary to the evidence from several studies of oleic acid chlorination (2-5). These all indicate that in the temperature range under consideration, oleic acid can be chlorinated by both addition and substitution, the hydrogen atoms adjacent to the double bond being the most readily replaced. Other possibilities exist, including polymerization with elimination of hydrogen chloride (6), but the consensus is that addition and substitution are the major reactions in dilute solutions.

EXPERIMENTAL PROCEDURES

Since preliminary work confirmed beyond doubt that hydrogen chloride is produced in the reaction, some modification of Roper's technique was necessary. As shown in Figure 1, metered flows of the two reactants were mixed immediately before passing through a small tubular reaction chamber. Exit concentrations of chlorine and hydrogen chloride were determined by "quenching" a known weight of the reaction mixture in a vigorously agitated alcoholic solution of potassium iodide. The iodine liberated by the chlorine was estimated by standard titrametric methods using sodium thiosulphate solution, and the hydrogen chloride content was similarly determined using sodium hydroxide solution. Due allowance was made for the acidic effect of the oleic acid. Detailed product analysis, a difficult problem in a system such as this, was not attempted. The reactor residence time was varied between 0.22 and 1.44 sec, mainly by changing its length. Experiments were performed at 25, 35 and 44 C using reactant concentrations ranging from 0.026-0.119 gmole oleic acid/liter CCl_4 and 0.019-0.300 gmole Cl_2/liter CCl_4. A few experiments were conducted in darkness, but most runs were carried out under illumination provided by two 40 w

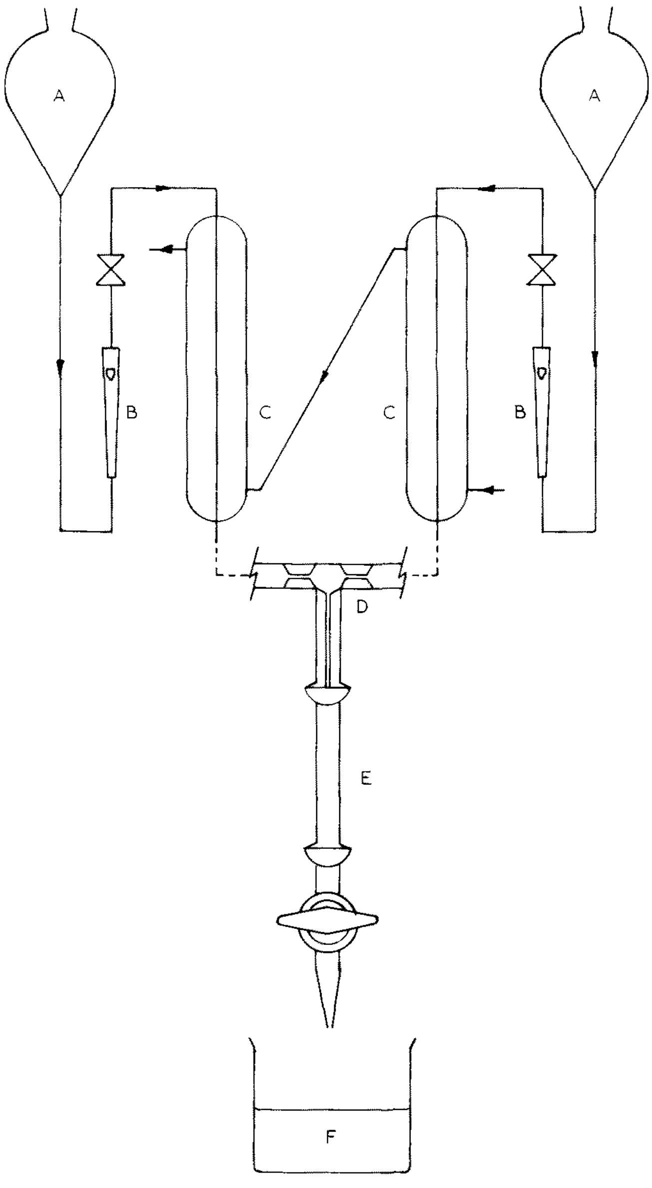

FIG. 1. Experimental apparatus. A, Feed tanks; B, rotameters; C, thermostats; D, mixing section; E, reactor body; and F, quench solution.

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[1] Nomenclature: a = concentration of oleic acid with double bond intact, gmole/liter; c = concentration of chlorine, gmole/liter; k = reaction rate constant, liter/gmole sec; $n = k_a/k_s$; $m = x_a/x_s$; p = constant defined by equation [6]; Q = constant defined by equation [7]; $Q_{1,2,3}$ = constants defined in equation [14]; s = concentration of oleic acid with substitution sites intact, gmole/liter; x = fractional conversion; $Y = c_o/(s_o + ma_o)$; $Z = c_o/a_o\ (m + 1)$. Subscripts: o refers to initial conditions; a refers to addition reaction; s refers to substitution reaction.

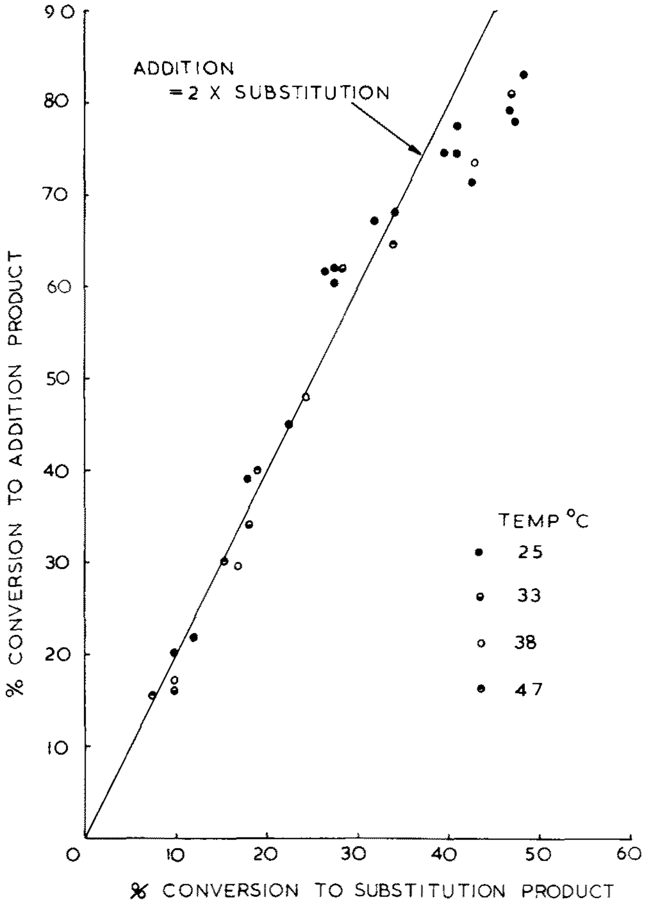


FIG. 2. Experimental product distribution data.

fluorescent strip lights placed at a distance of 2 ft on either side of the reaction chamber. In all cases care was taken to exclude the reactants from contact with metal of any kind.

RESULTS

Oleic acid is very difficult to prepare in a state of high purity, and gas liquid chromatography (GLC) analysis showed that the acid used in this study contained small amounts of other fatty acids. This has been accounted for in the results by using a molecular weight for the acid based on the degree of unsaturation. The value used is 292, the molecular weight of the pure acid being 282.

"Product Distribution" results are shown in Figure 2. In constructing this diagram it has been assumed that hydrogen chloride is produced exclusively by substitution reaction, the balance of the chlorine depletion being due to addition. It indicates that the ratio of addition to substitution is approximately linear up to 70% conversion to the addition product, and that this ratio is unaffected by temperature in the range 25-44 C. Note that "% conversion to addition product" signifies the proportion of oleic acid which has been involved in an addition reaction, producing either a simple addition product or an addition-substitution product. "Conversion to substitution product" is to be interpreted in a similar way.

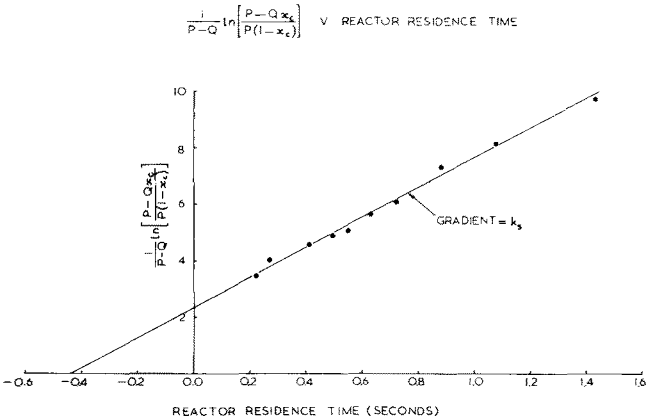


FIG. 3. The interpretation of experimental data for independent parallel reactions $\frac{1}{P\text{-}Q}\ln\left[\frac{P\text{-}Qx_c}{P(1\text{-}x_c)}\right]$ vs. reactor residence time.

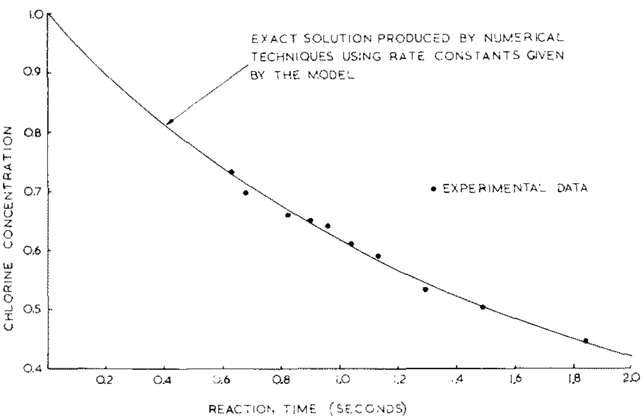
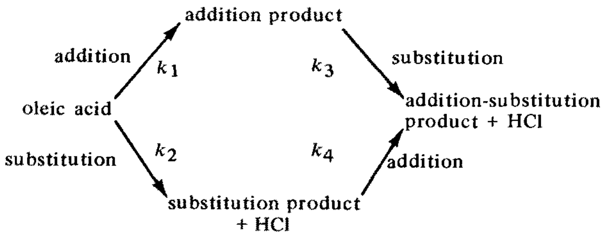


FIG. 4. The variation of chlorine concentration with time for the interdependent parallel reaction regime.

Plots of reactant concentration vs. reactor residence time for this type of experiment are complicated by an "end effect" caused by the time required to completely quench the reaction mixture. In a fast reaction system such as this, appreciable conversion must take place in the plume of reaction mixture which extends a small distance below the surface of the agitated quench liquid. For this reason, it is convenient to present such plots following the development of kinetic models for the reaction system.

Kinetic Models

It seems clear that the main features of any kinetic model for this system must be the parallel addition and substitution reactions. In developing a model, only these possibilities will be considered, and it will be taken that both types of reaction can be represented by irreversible, second-order kinetic equations. It is known that the true mechanism of these reactions is complex, and involves free radicals. Nevertheless chlorination kinetics have often been handled successfully by simple second-order kinetic models, e.g., the chlorinations of benzene and methane. A further assumption will be that only mono substitution is significant. Since there is approximately twice as much addition as substitution, this supposition would appear reasonable, especially at low conversions. The reaction model may then be represented as:



This scheme may be simplified considerably if it is assumed that prior occurrence of one reaction has no effect on the other. In this case we may write $k_1 = k_4 = k_a$ and $k_2 = k_3 = k_s$, reducing the system to a simple independent parallel reaction:

oleic acid with double bond intact (although possibly substituted) $+ Cl_2 \xrightarrow{k_a}$ products

oleic acid with substitution sites intact (although possibly added) $+ Cl_2 \xrightarrow{k_s}$ products

For second-order reactions, there is no analytical solution for this model, although solutions can of course be determined numerically. However, for this particular system, the observed linearity of the product ratio data (Fig. 2) allows an approximate analytical solution to be derived

Approximate Analytical Solution for an Independent Parallel Second-Order Reaction Regime

Let: c = concentration of Cl_2; a = concentration of oleic acid with double bond intact; s = concentration of oleic acid with substitution sites intact; $n = k_a/k_s$. Then the rate of consumption of Cl_2 is:

$$-\frac{dc}{dt} = k_a ac + k_s sc = nk_s ac + k_s sc \qquad [1]$$

In terms of fractional conversions:

$$c = c_o(1 - x_c)\ ;\ a = a_o(1 - x_a)\ ;\ s = s_o(1 - x_s) \qquad [2]$$
$$c_o \frac{dx_c}{dt} = nk_s a_o(1 - x_a)c_o(1 - x_c) + k_s s_o(1 - x_s)c_o(1 - x_c)$$

When the product ratio is constant: $x_a = m\ x_s$; and by a chlorine balance: $c_o x_c = s_o x_s + a_o x_a$; from which: $x_s = \dfrac{c_o x_c}{s_o + ma_o}$. Substituting for x_a and x_s in equation [2]:

$$c_o \frac{dx_c}{dt} = nk_s a_o c_o(1 - x_c)(1 - \frac{mc_o x_c}{s_a + ma_o}) + k_s s_o c_o(1 - x_c)(1 - \frac{c_o x_c}{s_o + ma_o}) \qquad [3]$$

Dividing by c_o and putting $\dfrac{c_o}{s_o + ma_o} = Y$:

$$\frac{dx_c}{dt} = nk_s a_o(1 - x_c)(1 - mYx_c) + k_s s_o(1 - x_c)(1 - Yx_c) \qquad [4]$$

Multiplying out and collecting terms according to the power of x_c:

$$\frac{dx_c}{dt} = k_s[P - (P + Q)x_c + Q x_c^2] \qquad [5]$$

$$\text{where}\quad P = s_o + na_o \qquad [6]$$

$$\text{and}\quad Q = s_o Y + mna_o Y \qquad [7]$$

Then

$$\int \frac{dx_c}{(P - Qx_c)(1 - x_c)} = k_s \int dt \qquad [8]$$

which gives

$$\frac{1}{P-Q} \ln\left[\frac{P - Qx_c}{P(1 - x_c)}\right] = k_s t \qquad [9]$$

Hence, if m and n are known, the reaction rate constants can be determined from the variation of the chlorine concentration, x_c, with time.

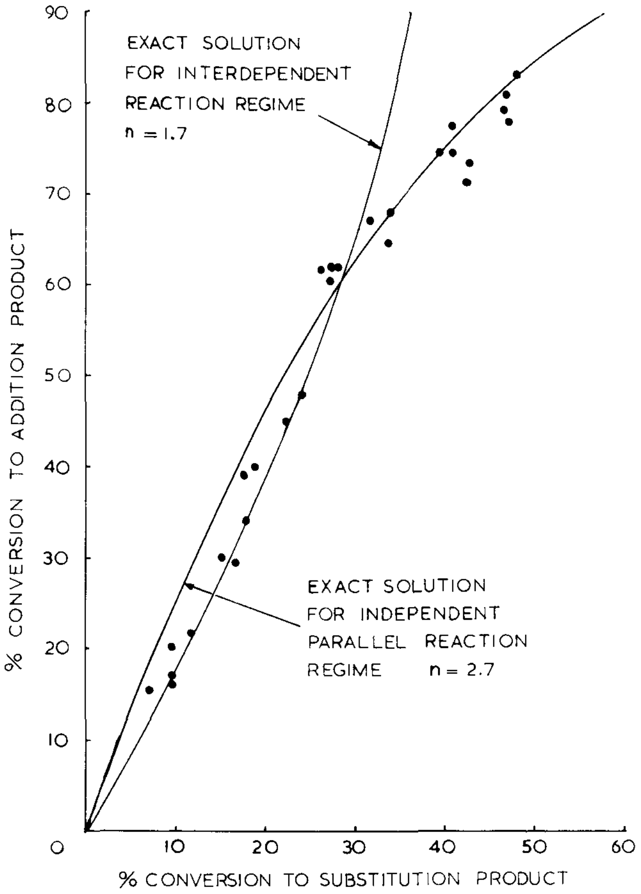


FIG. 5. Comparison of experimental product distribution data with the solutions for independent and interdependent parallel reaction regimes.

For this model, the ratio of the rate constants, n, may be obtained from the product distribution data as follows:

$$-\frac{da}{dt} = k_a ac \qquad [10]$$

$$-\frac{ds}{dt} = k_s sc \qquad [11]$$

Dividing [10] by [11]

$$\frac{da}{ds} = \frac{k_a}{k_s}\frac{a}{s}$$

$$\ln a = \frac{k_a}{k_s} \ln s + \text{constant} \qquad [12]$$

Thus a log plot of the concentration of acid available for addition against that of acid available for substitution should yield a straight line of slope n if an independent, parallel second-order reaction system is operating.

Approximate Analytical Solution for an Interdependent Parallel Second-Order Reaction Regime

If the addition and substitution reactions are not independent of each other, the resulting model is more complex. In the chlorination of oleic acid, there is some evidence (4) that the addition reaction tends to block the substitution reaction. In terms of the kinetic model, this can be accounted for by putting $k_3 = 0$. A further assumption is now necessary in order to derive an approximate analytical solution. As well as taking the product ratio to be constant, it is necessary to assume that the amount of addition to previously substituted molecules is proportional to the total amount of substitution. Thus the concentration of acid with sites available for substitution is given by: $s =$

TABLE I

Temperature, C	Independent parallel reaction model		Interdependent parallel reaction model	
	k_a	k_s	k_a	k_s
25	12.8	4.7	12.4	7.3
35	13.9	5.1	13.1	7.7
44	15.8	5.9	14.8	8.7

$s_o - s_o x_s - a_o x_a(1 - x_s)$; and since $a_o = s_o$:

$$s = a_o(1 - x_s)(1 - x_a) \qquad [13]$$

Using similar methods to those used in the derivation of the previous model, the following solution may be derived (7).

$$Q_1 \ln(1 - x_c) + \frac{Q_2}{mZ} \ln(1 - mZx_c) + \frac{Q_3}{Z} \ln\left(1 - \frac{Zx_c}{1+n}\right) = -a_o k_s t \qquad [14]$$

where $Q_1 = \dfrac{1}{(1 - mZ)(1 + n - Z)}$; $Q_2 = \dfrac{1}{\left(1 - \frac{1}{mZ}\right)\left(1 + n - \frac{1}{m}\right)}$; $Q_3 = 1 - (n + 1)(Q_1 + Q_2)$; $Z = c_o/a_o\,(m + 1)$. In this model

$$\frac{da}{ds} = \frac{k_a a_o (1 - x_a) c_o (1 - x_c)}{k_s a_o (1 - x_a)(1 - x_s) c_o (1 - x_c)} \qquad [15]$$

$$x_a = \frac{-k_a}{k_s} \ln(1 - x_s) \qquad [16]$$

and so the value of n can be found from a plot of x_a against $-\ln(1 - x_s)$.

The main usefulness of the above approximate solutions in the present system is that they provide a basis for linear plots of data. These can then be used to interpret experimental end effects and estimate the values of the reaction rate constants.

Interpretation of Experimental Results by the Approximate Solutions

Figure 2 shows that up to 70% conversion to the addition product, the product ratio m equals 2. Applying equation [12] to this product distribution data, the value of the rate constant ratio, n was found to be 2.7 for the independent parallel reaction model.

Concentration-time data may now be graphed using equation [9], and an example is shown in Figure 3. Good linear plots of this type were obtained for all experimental runs. The negative intercept on the time axis represents the experimental end effect, while the slope of the line gives the value of k_s.

For the interdependent parallel reaction model, equation [16] gives the value of n to be 1.7 and substitution of the concentration-time data in equation [14] again resulted in good linear plots. Table I summarizes the values of the reaction rate constants determined for the two models by applying the approximate solutions to the data. These data indicate activation energy values of 2000 and 1750 cal/gmole, respectively. The results of experiments conducted in the dark could not be distinguished from those obtained under conditions of illumination. This unexpected result would suggest that either the illumination intensity or contact time was below some necessary threshold value.

DISCUSSION

The approximate solutions for both kinetic models have been shown to fit the experimental concentration-time data well. Equally good agreement was found when these data were compared with exact solutions produced using numerical techniques. An example of this for the interdependent model is shown in Figure 4 where the exact solution has been generated using the rate constants obtained by the approximate solution.

The two kinetic models, however, predict somewhat different product distributions, as illustrated in Figure 5. At high conversions, the best fit of the data is achieved by the independent parallel reaction model, while the more complex model is superior at lower conversions.

On the basis of these data there is little justification for choosing between the models, but literature evidence suggests that the interdependent model is probably more realistic, i.e., the addition reaction blocks the substitution reaction by the formation of a stable structure, deactivating the substitution sites. On these grounds, and with some supporting experimental evidence (4), it is suggested that the interdependent parallel reaction model embodies the main features of the "overall" kinetics.

If polysubstitution is taken into account, the manner of application of the models is substantially unaltered. This follows from the method of defining reactant concentrations and conversions. The overall effect is to reduce k_s by a factor approximately proportional to the number of equally available substitution sites.

It is interesting to note that an almost linear curve is obtained when chlorine concentration-time data are plotted on second-order coordinates, probably explaining why Roper (1) reported simple second-order kinetics. Less satisfactorily, it has not been possible to explain conclusively why the sums of the parallel reaction rate constants found in the present work are an order of magnitude lower than the second-order reaction rate constants reported in the previous study.

As far as is known, oleic acid quality was similar in both cases, but as the initiation and termination reactions can be influenced strongly by impurities in the reaction mixture, it may well be that a slight difference in composition caused this discrepancy. Such reactions can also be influenced by reactor materials and dimensions, which again, as far as can be determined, were similar. The only apparent differences are our use of illuminated conditions, and rather higher chlorine concentrations, both of which seem unlikely to be the cause of lower reaction rate constants. It was thought that hydrogen chloride production might have affected Roper's analytical technique, but tests showed that this was not the case.

It is an unfortunate fact that different studies of the same free-radical reaction have, not uncommonly, reported considerably different rates.

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