[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Kinetic Measurements in a Stirred Flow Reactor; the Alkaline Bromination of Acetone[1]

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Denbigh[2] has shown that the *instantaneous rate* of a chemical reaction can be measured by what amounts to balancing the reaction rate against a rate of flow of liquid in a self-maintaining steady state. For this purpose reactants are introduced at a constant flow rate u into a reactor of fixed volume V in which there is thorough stirring, and a homogeneous partly reacted mixture is removed at essentially the same rate. Such a system reaches a steady state in which all concentrations remain unchanged indefinitely and returns to the same state if it temporarily displaced from it. In this steady state the rate r of formation of *any* reactant, intermediate or reaction product is given by

$$r = (u/V)(c - c_0) \tag{1}$$

Here c is the concentration of the substance in the steady state and c_0 its concentration in the entering liquid, and the disappearance of a reactant or intermediate by reaction is taken as a negative formation. The validity of (1) for any substance is not impaired by the presence of competing or consecutive reactions.

The Denbigh technique has obvious advantages over the usual measurement of *quantity reacted in finite time* if the reaction is complex or if, because of changes in the nature of the medium with progressing reaction, its rate deviates from exact proportionality to concentration of reactants. Its most obvious disadvantage is that reagents must flow to waste during the establishment of the steady state and the measurement of the steady state concentrations. We report herewith a study of the application of this technique to a reaction for which the advantages are of prime importance and show that, even for a complicated reaction system, the wastage of reagents is not excessive.

Symbols.—We use the following symbols in this and the immediately following papers.

a, b, c	Concentrations of reactants in the reactor at steady state
x, y	Concentrations of reaction products in the reactor at steady state
a_0, b_0, c_0	Concentrations of reactants in the entering liquid
x_t, y_t	Concentration of reaction product at time t
t	Time
u	Total flow rate
V	Reactor volume
η	Degree of conversion in the steady state, *i. e.*, x/a_0 or x/b_0 whichever is larger
τ	No. of multiples of the reactor volume which have traversed the system, *i. e.*, tu/V
ρ	a_0/b_0
r	Rate of reaction
k, k'	Rate constants

All times are in minutes, volumes in liters, concentrations in mole/liter. In the present paper a refers to acetone, b to sodium hydroxide, c to hypobromite, x to bromoform and y to carbon tetrabromide.

Approach to the Steady State.—The basic equation is

$$\frac{dx_t}{dt} = r - \frac{ux_t}{V} \tag{2}$$

The stoichiometric equation for the bromination of acetone is usually considered to be

$$(CH_3)_2CO + 3BrO^- \longrightarrow CHBr_3 + CH_3CO_2^- + 2OH^- \tag{I}$$

and the rate has been found to be proportional to the concentrations of acetone and hydroxyl ion and independent of the concentration of hypobromite ion.[3] The reaction is therefore autocatalytic and of zero order with respect to one reactant. Neither (I) nor this rate expression are exact, as will be shown, but they are a good enough approximation for the following considerations of the approach to the steady state. On this basis

$$r = kab = k(a_0 - x_t)(b_0 + 2x_t) \tag{3}$$

In the steady state $dc/dt = 0$, hence

$$k = \frac{u}{V}\,\frac{x}{(a_0 - x)(b_0 + 2x)} \tag{4}$$

and in terms of η and ρ

$$k = \frac{u}{Va_0}\,\frac{\eta}{(1 - \eta)(\rho + 2\eta)} \tag{5}$$

The variables of interest are τ and x_t/x, and in terms of these (2), (3) and (5) reduce to

$$\frac{d(x_t/x)}{d\tau} = \frac{\rho + (2\eta^2 - \rho)(x_t/x) - 2\eta^2(x_t/x)^2}{(1 - \eta)(\rho + 2\eta)} \tag{6}$$

The integral is known and the constant may be derived from the fact that in our experiments the reactor is initially full of unreacted reagents so that when $\tau = 0, x_t = 0$. From this

$$\tau = \frac{(1 - \eta)(\rho + 2\eta)}{\rho + 2\eta^2} \ln \frac{\rho + 2\eta^2(x_t/x)}{\rho(1 - x_t/x)} \tag{7}$$

Curve A of Fig. 1 plots the values of $\tau_{0.001}$, the number of multiples of the reactor volume which must flow through the system in order to bring the product concentration to a value differing

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* Harvard College A.B. 1916.

(1) Based on part of a dissertation submitted by Harrison H. Young, Jr., in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University.

(2) (a) Denbigh, *Trans. Faraday Soc.*, **40**, 352 (1944); (b) Stead, Page, and Denbigh, *Faraday Soc., Discussions* No. 2, 263 (1947); (c) Denbigh, Hicks and Page, *Trans. Faraday Soc.*, **44**, 479 (1948).

(3) Bartlett, THIS JOURNAL, **56**, 967 (1934).

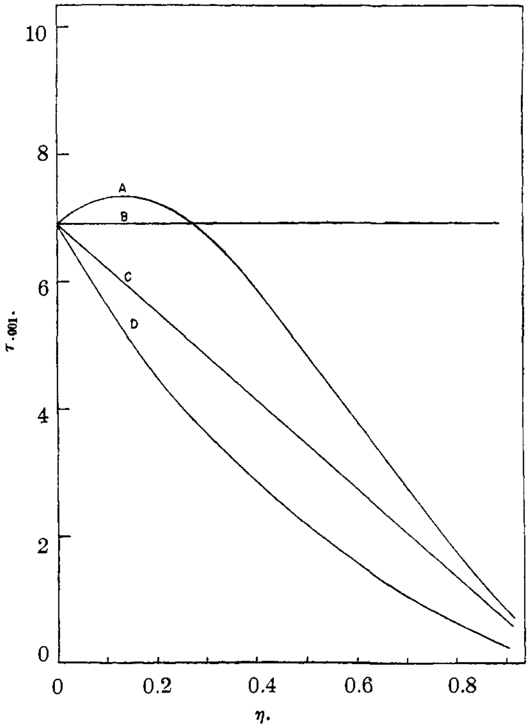

Fig. 1.—Approach to the steady state. Displacements to attain $x_t/x = 0.999$, reactor initially full: A, alkaline bromination of acetone, $\rho = 1$; B, zero-order reaction; C, first-order reaction; D, second-order reaction, $\rho = 1$.

by only 0.1% from the steady state, *i. e.*, to make $x_t/x = 0.999$. The plot is for $\rho = 1$, but it does not differ much for values of ρ in the range of our experiments, from 0.9 to 2.3. Figure 1 also contains similar plots for other reaction orders. The relevant equations may be derived by the method used in obtaining (7) and are equivalent to equations given elsewhere.[1,4] The conclusion that the steady state condition may be reached to a high precision with the expenditure of a volume of reagent little over seven times the reactor volume in the most unfavorable case and frequently of a materially smaller volume is not unfavorable to the practical usefulness of the Denbigh technique.

Consecutive Reactions in the Stirred Flow Reactor.—If (I) and (3) were a complete account of the bromination of acetone the η of (5) would be given by

$$\eta = (c_0 - c)/3a_0 \qquad (8)$$

and the rate constant k would follow immediately. It is, however, known[5] that bromoform reacts slowly with hypobromite. Considering both the formation of bromoform and its further reaction the steady state equation for its concentration x is

$$(u/V)x = k(a_0 - x - y)(b_0 + 2x + 3y) - k'x \qquad (9)$$

while that for the steady state concentration of carbon tetrabromide y is

$$(u/V)y = k'x \qquad (10)$$

Further

$$c_0 - c = 3x + 4y \qquad (11)$$

From (9), (10) and (11) we obtain

$$k = \frac{u}{V}\,\frac{x(1 + k'V/u)}{[a_0 - x)(1 + k'V/u)][b_0 + x(2 + 3k'V/u)]} \qquad (12)$$

with

$$x = \frac{c_0 - c}{3 + 4k'V/u} \qquad (13)$$

Since k' may be determined by a separate experiment on the rate of bromination of bromoform, the rate constant k of the first step in this system of consecutive reactions of complicated order may be determined by substitution of easily obtainable experimental quantities in an explicit formula (12). And indeed if the order of this step were completely unknown it could be easily investigated since its rate r is given by

$$r = \frac{u}{V}(c_0 - c)\,\frac{1 + k'V/u}{3 + 4k'V/u} \qquad (14)$$

and the experimentally observed dependence of this rate on the concentrations of reactants would make it possible to determine the reaction order. Although the present case is one in which consideration of the second step leads only to a small correction there is nothing in the derivation of (12) and (14) which limits them to such a case. The determination of reaction orders and rate constants in a system of consecutive reactions of order higher than one offers therefore no special difficulty in the method of the stirred flow reactor; it has been an extraordinarily difficult problem when approached by the conventional batch method of investigating reaction kinetics.

Experimental

Apparatus.—We have obtained a constant flow of reagent solutions by forcing them from reservoirs through capillaries into the reactor by means of a constant pressure of air, the whole system being immersed in a thermostat at 25.00°. The Pyrex reservoirs, capillaries and reactor are shown in Fig. 2. The air pressure system was in principle that shown in the following paper.[6] The air line

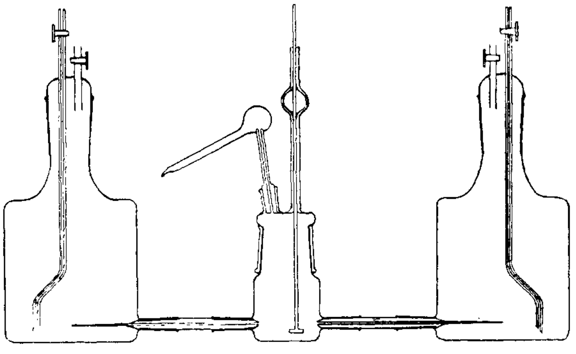

Fig. 2.—Continuously flowing reaction system, showing reaction cell with reagent reservoirs attached.

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[4] Harris, *J. Phys. Colloid Chem.*, **51**, 505 (1947).

[5] (a) Fuson and Bull, *Chem. Revs.*, **15**, 275 (1934); (b) Dehn, THIS JOURNAL, **31**, 1220 (1909).

[6] Saldick and Hammett, *ibid.*, **72**, 283 (1950).

to the alkaline hypobromite solution contained a soda-lime tube to remove carbon dioxide, which not only changed the alkalinity of the solution, but also altered its viscosity and flow rate. The capillaries were of non-uniform inside dimensions; suitable ones were obtained by cut and try. It is important that capillaries and reservoirs be thoroughly cleaned with dichromate–sulfuric acid between runs. With this precaution and barring easily recognizable blocking due to particulate matter, the flow rate of a single reagent can be held constant to about ±0.1%. With both reagents flowing deviations were greater, but in only one case was it more than 1%. The air-driven stirrer was made of stainless steel. So far as could be judged from the behavior of a fine suspension of sawdust particles, agitation and mixing were excellent. The volume of the reactor with capillary tubes and stirrer in place was 0.118 ± 0.1 liter. No evidence of back diffusion from reactor into the capillaries was observed when one reservoir contained dilute alkali, the other phenolphthalein solution.

Materials.—Selection of materials, preparation of reagent solutions, standardization of solutions for titration and calibration of equipment met customary standards for precision work. The concentration of acetone in the reagent solution was determined by the Messinger method.

Total bromine in the hypobromite solution was determined by adding 10 ml. of 2 *M* potassium iodide and 3 to 3.5 ml. of concentrated hydrochloric acid to the sample and diluting to 50 ml. The acid is required to ensure reduction of bromate as well as hypobromite but it leads to air oxidation of the iodide. Consequently 25 ml. of 2.7 *M* sodium acetate solution was added to each sample to lower the acidity, thereby interrupting the oxidation, before titration with thiosulfate. The air oxidation was linear with time, for periods up to half an hour at least, so it was critically important to maintain the high acidity for the same interval of time in each sample among a set. This interval was observed within experimental limits of ± three seconds, and was in the order of five minutes, though between independent sets of samples, it ranged from three minutes to nine minutes. A blank under identical conditions accounted for impurities in the sodium acetate and for the air oxidation. The hydroxyl ion concentration of the hypobromite solutions was computed from the bromine titer thus obtained and the known titer of the sodium hydroxide solution from which the hypobromite was prepared by the addition of bromine. The total bromine titer did not change over several days and the slow conversion of hypobromite to bromate does not alter the hydroxyl ion concentration.

Method.—In making a run the reagent solutions contained in the reservoirs of Fig. 2 were brought to temperature and the flow rate of each reagent through the particular capillary and under the driving pressure to be used in the run was measured with the stirrer running, the flow of one being prevented while the other was being measured. The flow rate was determined by catching the overflow during several measured periods in tared flasks and weighing. A loose covering of the flask was shown to be sufficient to prevent significant evaporation. The density of each reagent was determined in order to compute the volume rate of flow.

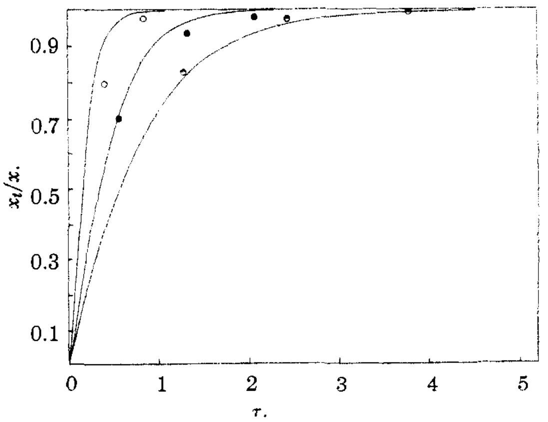

Fig. 3.—Approach to the steady state: curves represent theoretical variation of x_t/x with the number of turnovers for Runs 19, 17, 28; points are experimentally determined values, ○ for 19, ● for 17, ⊖ for 28.

With the flow stopped the reactor was then emptied by siphoning out the contents and was quickly refilled by introducing quantities of reagent solutions in proportions corresponding to their flow rates. The cap of the reactor was immediately replaced and the flow and stirrer started.

At suitable intervals a 20 to 35-g. sample of the overflow solution was caught in a tared flask containing 5 ml. of an acetic acid–sodium acetate buffer (0.052 mole of each per liter), which was then weighed. It was shown that reaction of bromine and acetone in the resulting mixture was negligible during any period which might precede the analysis. These samples were analyzed for bromine by the method previously described.

After the steady state had been reached one or more 25-ml. aliquots were quickly removed from the reactor and run into an excess of standard sodium arsenite solution. The hypobromite concentration of the solution was then determined by back titration with standard iodine solution in order to make certain that hypobromite and not merely bromate remained present in the solution. The density of the steady state solution was also determined but was always found to differ negligibly from that calculated from the densities of the reagents on the assumption of no volume change on mixing and reaction. The end concentration of bromoform, being of the order of 0.001 molar, was well below the reported solubility of the substance, and no precipitation was in fact observed.

Overflow Tube Correction.—The observed hypobromite concentration in the overflow solution was corrected to the value of the concentration in the reactor, the correction being necessary because of the small account of reaction which occurs while the solution remains in the overflow tube. The correction, made by the method of the next article,[6] amounted to 0.3% or less.

The Bromination of Bromoform.—Under the conditions of our experiments the total consumption of bromine by acetone rises from 6 equivalents at the end of one hour to 6.9 at twenty-two hours, 7.7 at seventy-seven hours, and 8.0 at one hundred and fifty and one hundred and ninety hours. From these we estimate a value of $k' = (1/x)\,dx/dt$ of 4.5×10^{-4}. Since this reaction leads only to a small correction in estimating k we have not attempted to obtain a more precise value.

Results and Discussion

The approach to the steady state is illustrated for three of our runs in Fig. 3. The smooth curves are plots of (6) with the appropriate values of η and ρ. The points are experimental and are in satisfactory agreement with the equation. The difficulties of applying the corrections for side-arm reaction and formation of carbon tetrabromide during the approach to the steady state obviated their use, but their effect would be small.

We have collected in Table I the pertinent data and results for fifteen runs in which a steady state was achieved. These embraced a variation in flow rate of nearly tenfold, and a variation in η of from 0.311 to 0.883. The rate constant k for the formation of bromoform was obtained from (12) and (13). At least two runs, in one case three runs, were made with a single lot of reagents, with the same flow rates, so as to obtain checking values. These are apparent in the

TABLE I

Run	10^3b_0	10^3a_0	ρ	10^3c_0	10^3c	10^3a	10^3b	u	η	k
13	1.720	1.890	0.91	5.04	1.50	0.716	4.090	2.758	0.621	9.37
14	1.720	1.890	0.91	5.04	1.49	.714	4.094	2.718	.622	9.27
16	1.930	1.593	1.21	6.35	2.87	.442	4.259	2.226	.723	11.53
17	1.930	1.593	1.21	6.35	2.88	.447	4.249	2.230	.719	11.40
18	1.665	1.500	1.11	6.60	2.59	.184	4.354	1.177	.877	16.38
19	1.665	1.500	1.11	6.60	2.57	.176	4.370	1.176	.883	17.16
20	1.665	1.500	1.11	6.60	2.57	.177	4.368	1.179	.882	17.10
21	2.410	1.048	2.30	8.40	5.85	.206	4.119	1.696	.803	14.26
22	2.410	1.048	2.30	8.40	5.85	.208	4.115	1.713	.802	14.25
23	2.124	1.599	1.33	6.40	3.40	.604	4.129	3.385	.622	11.45
24	2.124	1.599	1.33	6.40	3.32	.581	4.176	3.312	.637	11.78
25	1.980	1.492	1.33	6.94	5.55	1.028	2.911	10.143	.311	13.33
26	1.980	1.492	1.33	6.94	5.54	1.026	2.914	10.186	.312	13.45
27	2.666	1.649	1.62	5.92	3.70	0.909	4.151	7.550	.449	12.55
28	2.666	1.649	1.62	5.92	3.78	0.937	4.095	7.581	.432	11.92

tabulation. Although the agreement between these duplicate runs is good there is considerable variation in k over the whole range of measurements. We take this to indicate a real departure of the reaction from the accepted kinetics, and consider the observation of these phenomena to be an important indication of the merit of the flow method for rate studies.

Summary

The approach to the steady state in a stirred flow reactor agrees with theoretical prediction in a complicated reaction, the bromination of acetone. The consumption of reagents in the approach to the steady state is not so large as to be a prohibitive disadvantage in the use of the stirred flow reactor for rate measurements.

Rate constants for the successive steps in a system of consecutive reactions may be computed by substitution of easily accessible experimental quantities in explicit formulas, regardless of the order of the reactions.

The alkaline bromination of acetone in very dilute solutions deviates appreciably from accepted kinetics.

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Rate Measurements by Continuous Titration in a Stirred Flow Reactor[1]

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The present investigation is a study of an important advantage of the stirred flow reactor method[2] of investigating reaction kinetics in solution, namely the possibility of applying a scheme of continuous titration to the output of the reactor, thus avoiding the difficulty of quenching and analyzing a considerable volume of reaction mixture at an exactly known time.

The reaction employed for the development of the method was the alkaline hydrolysis of an ester. In the procedure used aqueous solutions of sodium hydroxide and of ester were introduced in separate streams of constant flow rate into a closed stirred reactor (Figs. 1 and 2); the partially reacted mixture overflowed from the reaction cell through a short exit tube to a small titration chamber, where it was mixed with a third *adjustable* flow of the titrating solution, which was aqueous hydrochloric acid containing acid–base indicator. The flow of the titrating solution was regulated until a visual end-point was observed.

Symbols.—In addition to those of the previous article[2] the following symbols are used. Units are the same as in that article. a refers to sodium hydroxide, b to ester, x to acid anion or alcohol.

x' Concentration of reaction product at point of titration
x'' Concentration of product at a point in the exit tube
t' Time a volume element of reaction mixture has spent in exit tube
V' Volume of exit tube

Experimental

Flow Measurements.—The solutions of reactants were driven from the 0.5-liter reservoirs C,C′ through glass capillaries P,P′ into the 0.03-liter reaction cell by *independent* constant pressure heads maintained in the air reservoirs B,B′ by the hydrostatic pressure between the constant-level device A and the openings of the J-tubes in the air reservoirs (see Fig. 1). The air used to drive the sodium hydroxide solution flow was passed through a soda-lime tube Q, and, when the ester used was volatile, the air used to drive the ester solution flow was passed through a

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* Harvard College A.B. 1916.

[1] Based on part of a dissertation submitted by Jerome Saldick in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University.

[2] Young and Hammett, THIS JOURNAL, **72**, 280 (1950). This contains references to Denbigh's pioneering reports on this technique.