ELECTROMETRIC STOPPED FLOW MEASUREMENTS OF RAPID REACTIONS IN SOLUTION

PART 1.—CONDUCTIVITY MEASUREMENTS

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An extension of the stopped flow, rapid mixing, method for studying fast chemical reactions in solution has been made, by the development of conductivity and glass electrode pH measuring techniques. The conductivity method of measuring the concentration of reactants has been extensively used to study the reaction $OH^- + CO_2 \rightarrow HCO_3^-$, and the results confirmed by optical, constant and stopped flow techniques. An artifact due to the presence of gas dissolved in the solutions has been observed and investigated. When this is controlled, the velocity constants obtained at various temperatures, by the different methods, can be expressed by

$$\ln k = 31{\cdot}30 - (13210/RT).$$

The use of electrical conductivity measurements with the rapid mixing method, for observing fast chemical reactions in solution, has been restricted to the work of Saal.[1] His technique was to measure the conductivity between two 0·8 mm platinum wires sealed in an 8 mm Jena normal glass observation tube, while the reacting mixture flowed by at a constant velocity as in the original Hartridge-Roughton [2] experiments. One major disadvantage of the constant flow method is the large expenditure of reagents. The stopped flow method introduced by Roughton[3] and later the use of electronic techniques for rapid recording by Chance[4] largely overcame this problem but the system has so far been restricted to spectrophotometric observations. The method to be described is a further extension of the stopped flow system by the application of conductivity measurements with rapid recording.

EXPERIMENTAL

Normally, the measurement of the conductivity of a solution is achieved by the use of a bridge network and an a.c. supply, the bridge compensating for supply voltage fluctuations and the a.c. reducing polarization effects on the electrode surfaces. In this problem, measurements are required within a few msec and the technique of bridge balance becomes impossible so a simpler network is used with a constant voltage supply. The speed of response and accuracy of measurements demanded by stopped flow techniques also requires that all polarization effects should be eliminated as far as possible and this presents the major problem in design. Polarization effects are mainly influenced by the size, shape and spacing of electrodes, the current passed, and the frequency and symmetry of the a.c. supply. The first of these factors is already limited by the necessity of arranging the electrodes to fit into a 3 mm diam. observation tube so particular attention has been paid to the other two. Another necessary is that the electrodes should be made of a chemically inert material; platinum or stainless steel have been found the most suitable. Finally the frequency of the a.c. supply should be such that it can be modulated up to frequencies of the order 1 kc/sec if a rapid change in conductivity is to be followed.

The apparatus consists of a constant voltage 50 kc/sec oscillator, an electrode supply and calibration network, the rapid reaction chamber and electrode system, an a.c. amplifier which is followed by a rectifier and filter, and finally a d.c. amplifier and cathode-ray oscilloscope. Traces appearing on the c.r.o. were recorded photographically.

The oscillator is based on a circuit described by Johnson,[5] and later modified by Booth.[6] Provision was made for exploratory measurements over the frequency range 2-50 kc/sec, with an extra high frequency of 300 kc/sec available for polarization checks. These observations showed that a frequency of 50 kc/sec met the conditions stipulated earlier and all the kinetic data given later were recorded at this frequency. The electrode network, a.c. amplifier and detector are shown in fig. 1. The 50 kc/sec constant voltage supply is fed into a voltage control VR_1, and then via a sensitivity control VR_2, to the electrode cell. The variation in voltage across the cell is dependent on the applied voltage via VR_1 and on VR_2, being maximum when VR_2 is equal to the cell impedance. The applied voltage is kept as small as possible, consistent with the gain required, in order to reduce the current across the cell and keep polarization effects small. The maximum current used is of the order of 1 mA, and the average 250 μA. The output from the cell is fed to an a.c. amplifier using a DL 91 pentode and then to an EA 50 rectifier, after which it is passed through a filter to a standard Cossor d.c. oscilloscope. Measurements have also been made on a separate d.c. amplifier with similar results. The advantages of the a.c. method are elimination of some comparatively small slow d.c. effects when the solution is pushed down the observation tube, and higher gain.

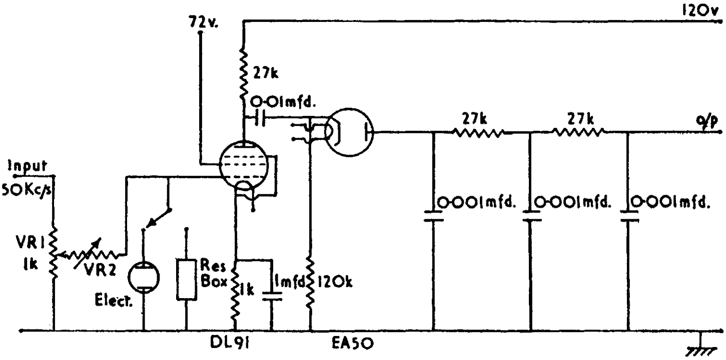

FIG. 1.—Electrode network, amplifier and detector.

The rapid reaction apparatus is built round a Perspex mixing chamber similar to those used by Chance [4] and is illustrated in plate 1. The chemical reactants are fed from two containing vessels, via three-way taps, to two 2 ml, all-glass syringes. The taps are then orientated so that when the two syringes are driven up together by a sliding platform, the reactants are driven into the Perspex mixing chamber and observation tube. The mixing chamber is based on the system of symmetrical tangential jets, in this case four of 1·5 mm diam., which feed into a 3 mm diam. observation tube. At 12 mm from the mixing chamber two tapped 1·2 mm diam. stainless steel electrodes have been screwed into the Perspex block on either side of the observation tube. All external electrical connections from these electrodes have been coated with Hi-meg varnish so that no electrical leakage occurs when the assembly is placed in a water bath to keep the temperature constant. A thermocouple has also been let into the observation tube about 1 mm after the electrodes so that the temperature of the reacting solution can be measured to within ± 0·2 °C. At the outlet of the observation tube a further 1 ml all-glass syringe, together with a Pyrex tap, have been arranged to provide a stopping mechanism similar to that used by Gibson.[7] For each individual run a maximum of 0·5 ml of solution is required.

Before proceeding to measurements on actual reactions the electrode system was calibrated with KCl and NaCl solutions to ensure consistency and discover the magnitude of polarization effects. Within the accuracy of the calibration resistance box used, which tended to show inductive and capacitative effects at 50 kc/sec, the results were consistent from solution to solution and polarization effects only become pronounced at the higher conductivities and at concentrations above 0·075 M. A value of 2·3 was obtained for the cell constant of the system.

APPLICATION

Though the apparatus was designed for a general investigation of fast reactions in solutions which could be observed by conductivity measurements, the present application has been restricted to recording kinetic changes of the reaction $CO_2 + OH^- \rightarrow HCO_3$.

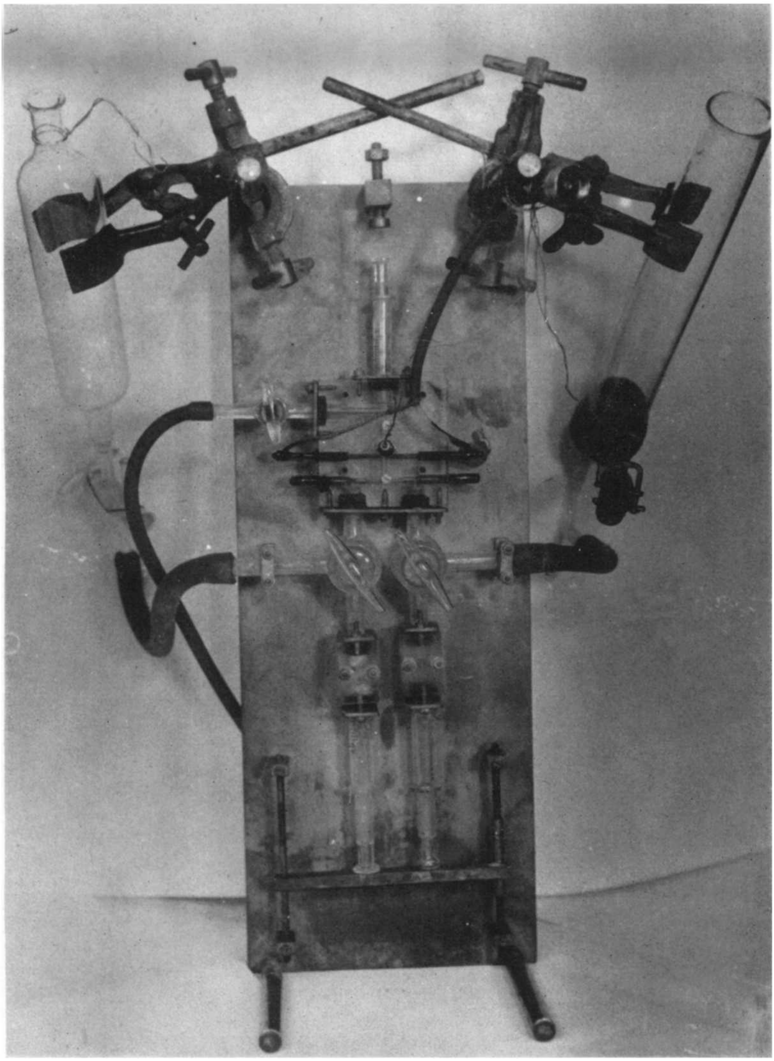

PLATE 1.

[*To face page* 202.

The mechanism of this process was formulated by Faurholt,[8] later confirmed and extended by Brinkman, Margaria and Roughton.[9] Further measurements of the kinetic constants were made manometrically by Pinsent and Roughton,[10] optically by Forrest,[11] and more recently, an extensive series of thermal data has been published by Pearson, Pinsent and Roughton.[12] The data obtained using the optical method showed significant differences from the results of the other methods. The conductivity apparatus has been used to investigate this discrepancy.

A series of measurements on the $CO_2 + OH^-$ reaction, were made with the conductivity apparatus over a range of temperatures and concentrations. The results showed consistent and significant deviations from those obtained thermally,[12] and appeared to be in agreement with the preliminary data obtained photo-electrically by Brinkman, Margaria and Roughton.[9] The latter results were obtained under relatively restricted conditions and their validity was not fully investigated at the time. A further series of experiments was therefore made with the constant flow photo-electric technique of Dalziel[13] and the stopped flow method of Gibson,[7] to confirm and extend the data.

The experimental conditions of temperature and concentrations were varied systematically and controlled for each of the techniques. The temperature was varied within the limits 0° C to 25° C with the conductivity system and 0° C to 35° C for optical measurements. The NaOH concentrations were changed from 0·02 M to 0·05 M and the CO_2 concentration from 0·005 M to 0·03 M. To follow the hydrogen ion change optically an indicator, Tropaeolin 0 at a concentration of $6{\cdot}8 \times 10^{-5}$ M, was added to the solutions. The wavelength of the light used was 5400 Å. In all cases the solutions were prepared from CO_2-free water obtained by double distilling then boiling at atmospheric pressure. The OH^- concentration was determined by titration with HCl, which in turn was standardized against Na_2CO_3. The CO_2 concentration was determined just before and after each experiment by making measurements on a 1 ml sample with the Van Slyke gasometric technique.

Each system was calibrated with appropriate mixtures of NaOH and Na_2CO_3, measurements having previously been made with the conductivity apparatus to ensure the effect of the dissolved CO_2 was negligible.

RESULTS

The velocity constant for the reaction was calculated from the data using the formula developed by Brinkman, Margaria and Roughton[9] based on the mechanism proposed by Faurholt.[8] The results obtained, for both the conductivity and photo-electric techniques, were significantly lower than the values obtained thermally.[12] Another discrepancy, in that the reaction curves showed an apparent instantaneous loss of OH^- concentration, was also observed. A further check on the mixing efficiency and calibration of the instruments revealed no significant errors. The possibility of an alternative chemical mechanism was also thoroughly investigated but no theory could be formulated to agree completely with the experimental facts. Eventually the discrepancy was traced to the presence of dissolved gas in the solutions.

EFFECT OF DISSOLVED GASES ON RAPID FLOW MEASUREMENTS

The curves in fig. 2 show the effect of saturating all the reacting solutions with a given inert gas. They represent the change of OH^- concentration, observed photo-electrically with the Dalziel constant flow system, at different distances along the observation tube from the mixing point. The initial loss in OH^- concentration, for the solutions equilibrated with air, corresponds to an incremental optical density change of 10^{-2}. The discrepancy from the expected initial point is dependent on the amount of gas dissolved and at low concentrations increases in proportion to the solubility of the gas used. Other gases, such as N_2O, have been used with similar results.

A series of blank experiments using equal concentrations of potassium dichromate in the supply bottles with different combinations of dissolved gases, such as O_2 and N_2O or N_2O and CO_2, did not show any optical density change. Potassium dichromate is convenient because of its relative chemical inertness and the ease by which various conditions of light absorption can be simulated by altering the wavelength. The addition of NaOH to all the solutions, in the absence of CO_2, also had no effect on promoting bubble formation with the various gases. It would appear that the formation of bubbles in the present experiments is dependent on the presence of both CO_2 and OH^-. Other gases in solution appear to magnify rather than initiate the process. An excess of CO_2, for instance, with all other gases excluded, can be shown, by extrapolation to the mixing point, to produce a similar optical density difference. The maximum CO_2 dissolved that can be tolerated is of the order one quarter saturated in the mixed solution. Apart from the fact that the effect can be magnified by various gases, proof that the discrepancy is due to a physical rather than a chemical action has been obtained by using a differential optical system which cancels out these effects.

The mechanism of the artifact is thought to be similar to the process of cavitation, the pressure changes and turbulence of the mixing and flow of solutions giving rise to small gas bubbles via minute gas nuclei. These bubbles cause an increase of the transmitted light in the photo-electric system and a corresponding decrease in conductivity. Thermal measurements, however, are almost completely unaffected by this process, the cooling produced by bubble formation in a large volume of moving fluid being extremely small.

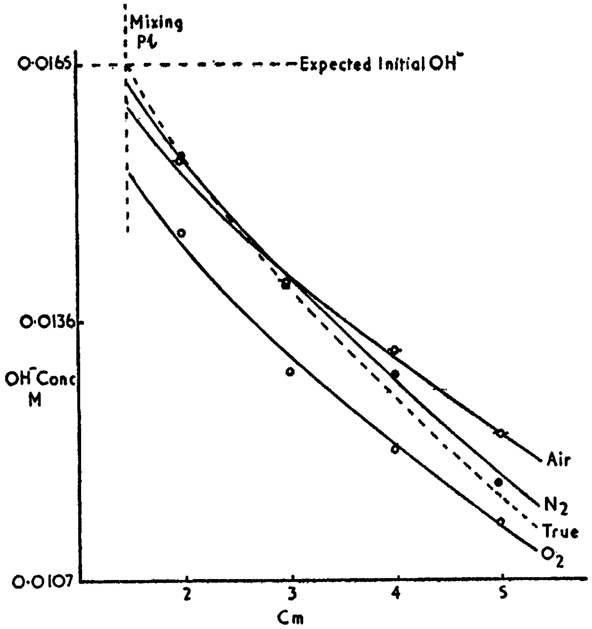

FIG. 2.—Typical reaction curves, obtained with the Dalziel technique, showing effect of dissolved gases. Conc. OH^-, 0·0165 M, conc. CO_2, 0·0049 M, in mixed solution; temp. 15·3° C; flow rate 295 cm/sec.

To avoid the artifact care has been taken in building the apparatus to eliminate any constrictions and variation of the diameter of the solution flow system and reduce unnecessary turbulence. Dean [14] has suggested that the presence of vortices in turbulent systems is the main cause of bubble formation and the experiments of Chance [4] with semi-tangential jets tends to support this. The essence, however, of the rapid moving and flow method is the generation of pressure changes and turbulence and it is doubtful if this factor can be effectively reduced without affecting the mixing efficiency. Prior to each experiment, all gas was removed from the solutions by evacuation. One solution was then one quarter or less saturated with CO_2. A driving gas, having as low a solubility as possible, was then applied. For the results given below N_2 was used, but care was taken to keep the solutions under reduced gas pressure until just before the experiment was started. The effect of any extraneous gas dissolved in the solutions under these conditions was found to be negligible.

THE KINETICS OF THE $CO_2 + OH^-$ REACTION

Taking the precautions noted above a new set of observations was made of the $CO_2 + OH^-$ reaction over the range of concentrations and temperature previously specified. On the basis that the reaction proceeds by the mechanism

$$CO_2 + OH^- \rightarrow HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O,$$

the rate of the reaction is given by

$$d[CO_2]/dt = -k[OH^-][CO_2],$$

and this can be expressed quantitatively [8] as

$$kt = \frac{2\cdot303}{(b-2a)}\log_{10}\left\{\frac{b-2n}{a-n}\right\} + \text{constant},$$

where $a = [CO_2]$ and $b = [NaOH]$ at zero time, $n = [CO_3^{2-}]$ at time t, and k the velocity constant. The results calculated for the photo-electric and conductivity data, using this formula, are shown in table 1. A typical conductivity curve is shown in fig. 3. Each value is the average of several curves. The value of k obtained at the lowest temperature, with the photo-electric system, is not particularly accurate due to condensation occurring on the observation tube.

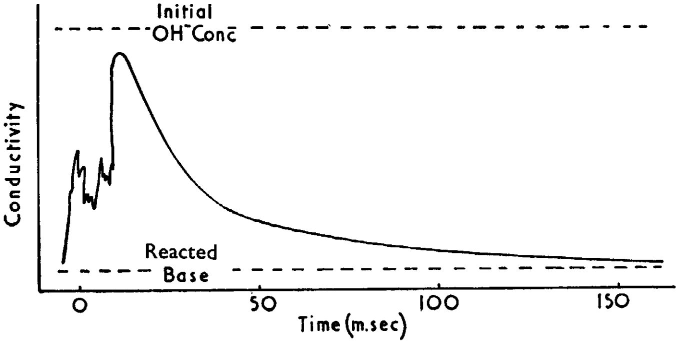

FIG. 3.—Typical conductivity reaction curve. Conc. OH⁻, 0·0129 M, conc. CO_2, 0·00353 M, in mixed solution; temp. 20° C.

TABLE 1

temp. °C.	mol. conc. OH^- (b)	mol. conc. CO_2 (a)	k	
3·3	0·0166	0·00472	975	photo-electric
11·0	0·0218	0·00426	3,310	
11·0	0·0163	0·00398	2,410	
16·3	0·0166	0·00575	4,570	
16·6	0·0201	0·00410	4,380	
20·7	0·0109	0·00249	5,590	
22·0	0·0163	0·00491	5,580	
27·0	0·0201	0·00437	10,150	
30·0	0·0109	0·00325	13,000	
2·7	0·0127	0·00467	1,260	conductivity
10·4	0·0130	0·00310	2,690	
11·6	0·0127	0·00225	3,350	
16·9	0·0127	0·00285	3,870	
20·0	0·0129	0·00353	5,000	

A plot of $\log_{10} k$ against the reciprocal of the absolute temperature is shown in fig. 4, for the optical and electrical conductivity results, and for comparison previous measurements by the thermal,[12] quenching,[8] and manometric[10] techniques. The slope of the line can be expressed by

$$\ln k = 31\cdot30 - (13{,}210/RT).$$

The excellent agreement between the five independent methods represents the most extensive and complete justification of the rapid mixing and flow method to date.

SCOPE AND ACCURACY OF THE CONDUCTIVITY MEASUREMENTS

The accuracy of the kinetic data obtained with the stopped flow conductivity technique is of the order ± 5 % and equivalent to the accuracy of the other methods of observations. The sensitivity of the apparatus has so far been restricted to reactions involving a 10 % overall change of conductivity, but providing the oscillator output is maintained correspondingly stable, this can be increased. The upper limit of usable conductance is of the order 0·01 mhos. Some extension of this limit can be obtained by using larger electrodes, but the onset of polarization effects is the deciding factor.

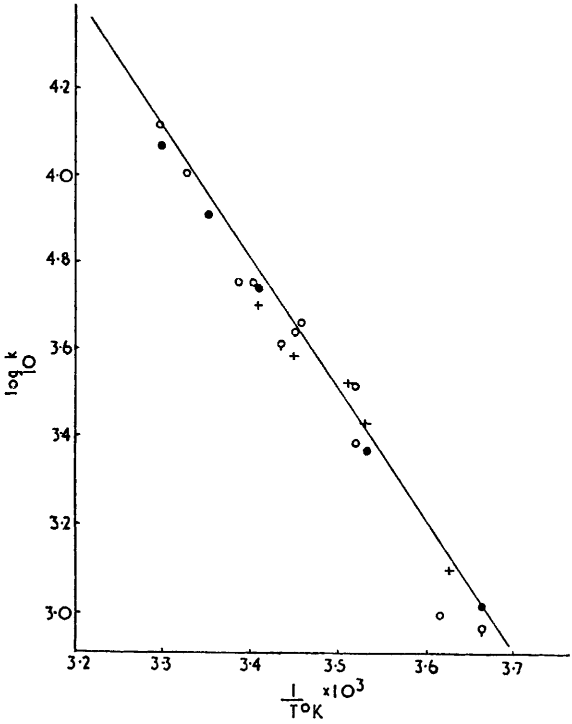

FIG. 4.—Comparative plot of the temperature dependence of velocity constant *k*, for the different methods.

— thermal ○ optical ● manometric
+ conductivity ♀ quenching.

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