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Note

Use of databases in the kinetic analysis of two parallel first-order reactions.
Part 2

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Abstract

Experimental and calculated values are compared in the analysis of two parallel first-order reactions. The method used here to obtain the two rate constants is less tedious and more rapid than the method of Brown and Fletcher.

INTRODUCTION

In a previous report [1] an expression (XP) was derived and utilized to ascertain concurrently the values of two rate constants for two parallel irreversible first-order reactions which afforded a common product (2PFC). Prior to the use of this XP, the procedure employed to estimate values of the two rate constants in 2PFC was indirect and rather tedious. In this regard, Brown and Fletcher [2] examined the hydrolysis of diethyl-*t*-butylcarbinyl chloride (DBC). Usually, a plot of the logarithm of the concentration of an unhydrolyzed alkyl chloride versus time yielded a linear relationship from whose slope the rate constant could be calculated. However, for the DBC used, no such relationship was observed. Instead, a first-order linear relationship was only found after a reaction time of approx. 2.5 h. This suggested that the unexpected behavior resulted from two simultaneous first-order reactions due to the presence of a mixture of two alkyl chlorides. One of these chlorides apparently hydrolyzed relatively rapidly and was essentially completely hydrolyzed at the end of approx. 2.5 h, whereas the other chloride hydrolyzed at a much slower rate. From the slope of the linear portion of the curve, a value of one of the rate constants could be estimated for the slower reaction. Then corrections of the experimental results could be made for the contribution of the slower reacting component, and a new set of rate data could be obtained from which the rate constant of the more reactive halide could be determined.

The XP previously mentioned involved the utilization of reaction rate measurements of slopes from a plot of the extent of reaction versus time, and was successfully applied to theoretical rate data. This XP was also applied to the experimental rate data of Brown and Fletcher for DBC [2]. In this latter case, an indirect approach was employed [1] in order to corroborate the validity of the XP and expressions used in its derivation. Thus, the XP was applied to rate data derived from the linear portion of the curve found by Brown and Fletcher [2] and yielded two rate constants which were almost identical. The average of these rate constants was in satisfactory agreement with that found by Brown and Fletcher. Then an expression utilized in the derivation of XP was also employed to ascertain the second rate constant value, which was also found to be in good agreement with that reported by Brown and Fletcher [2].

The aim of this paper is to utilize the XP and the raw data of Brown and Fletcher to ascertain concurrently the two rate constants for DBC. This method is less tedious and more rapid than that used by Brown and Fletcher [2].

RESULTS AND DISCUSSION

The 2PFC reactions can be represented as

$$\mathrm{A} \xrightarrow{k_1} \mathrm{C} + \ldots \tag{1a}$$

$$\mathrm{B} \xrightarrow{k_2} \mathrm{C} + \ldots \tag{1b}$$

where C denotes a common product (CP). This CP may, for example, consist of two different structural isomers which possess similar functional groups. Thus, concentrations of C could be determined by means of a quantitative analysis of such functional groups. Based on such values of C, the following expression (XP) was derived [1]

$$\ln\{[\rho - k_2(1-\alpha)]_0/[\rho - k_2(1-\alpha)]\} = k_1(t - t_0) \tag{2}$$

where α is the degree of conversion, t the reaction time, and $\rho = \mathrm{d}\alpha/\mathrm{d}t$. From eqn. (2), if the left-hand side is set to Y, then

$$Y = A_2X + A_1 \tag{3}$$

where $A_2 = k_1$, $X = t - t_0$ and $A_1 = 0$.

By utilizing eqn. (3) and the concepts of a computer algorithm previously devised and reported [1, 3–4], along with a Paradox 3 database script (PAL), values of k_1 and k_2 could be determined concurrently via an iterative procedure wherein a minimum value of A_1 was attained under the conditions employed.

A plot of α versus t (s) may be seen in Fig. 1 which used the experimental data of Brown and Fletcher [2]. From such a curve, various values of slopes

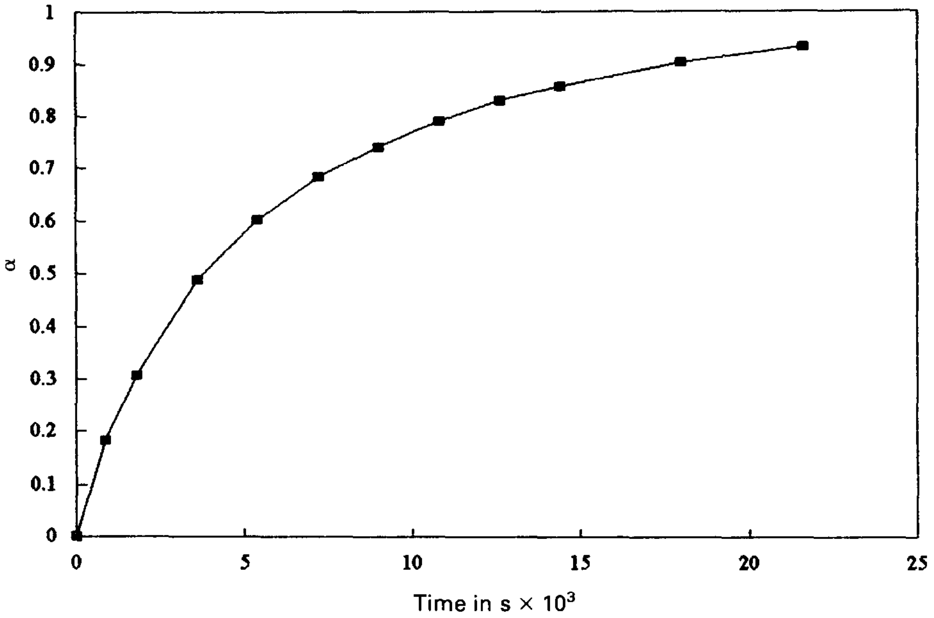

Fig. 1. Plot of α vs. time for DBC.

were carefully determined at various values of t. These values are listed in Table 1. From such values and the computer script previously noted, values of k_1 and k_2 (both in s^{-1}) were obtained, respectively: 4.46E − 04 (ref. 2, 4.39E − 04) and 1.06E − 04 (ref. 2, 1.05E − 04). The values at 1800 s in Table 1 were used as the subscript values for α, ρ and t in eqn. (2).

The preceding computer k-values were utilized to estimate values of α(calcd.), see Table 1. Prior to obtaining such values, it was necessary to

TABLE 1

Data for the hydrolysis of DBC

α	Time/s	Rate × $10^4/s^{-1}$ (from graph)	α(calcd.)
0.183	900		
0.308	1800	1.24	0.300
0.488	3600	0.750	0.478
0.603	5400	0.507	0.594
0.684	7200	0.418	0.676
0.743	9000	0.303	0.737
0.793	10800	0.220	0.785
0.831	12600	0.197	0.823
0.859	14400		0.855
0.905	18000	0.105	0.901
0.934	21600		

determine values of the original concentrations of the A and B components, i.e., $C(A_0)$ and $C(B_0)$, respectively. By utilizing values at $t = 1800$ s and eqn. (5A) of ref. 1, it was determined that $C(A_0)$ was very close to 1/3; thus, $C(B_0)$ was taken as 2/3 (ref. 2, $C(A_0) = 0.35$ and $C(B_0) = 0.65$. Then the various values of α(calcd.) in Table 1 could be calculated using eqn. (2) of ref. 1. The values of the experimental and calculated values of α are in reasonably good agreement. This agreement indicated that there was no reversal of *k*-values which was a possibility in the procedure employed [1].

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