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Use of databases in the kinetic analysis of two competitive, consecutive second-order reactions

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Abstract

In order to obtain the rate constants, k_1 and k_2, for two competitive, consecutive (series) second-order reactions (CCSR), previous workers have utilized approximate and graphical procedures. However, Frost and Schwemer (FS) were able to derive exact complex expressions, using a particular initial condition (to be described subsequently), which allowed tables of values pertinent to CCSR to be constructed. From such tables, values of k_1 and k_2 could be ascertained by the use of interpolation.

The aim of the present paper is to simplify the attainment of accurate values of k_1 and k_2 for CCSR by the utilization of cubic and quartic polynomial correlations based on the tables of FS. In this manner, and employing a database script (Paradox ver. 3.5), the preceding k-values could be obtained rapidly without the use of special tables and interpolations therefrom, and which agreed well with corresponding reported values. © 1997 Elsevier Science B.V.

Keywords: Kinetic; Analysis

1. Introduction

Ingold [1] used a method of successive approximations to obtain the values of the rate constants, k_1 and k_2, for two competitive, consecutive (series) second-order reactions (CCSR). Other investigators [2–4] utilized graphical procedures to ascertain such k-values. Frost and Schwemer (FS) [5] imposed, for convenience, an initial condition (IC) that $A_0 = 2B_0$ (equivalent amounts; also, A_0 and B_0 denote initial concentrations of reactants A and B, respectively) in order to derive rather complex and exact expressions which could allow accurate k-values to be obtained for CCSR. They also employed diminsionless variables in their derivations. Further, tables containing various derived data were devised which could allow the determination of the k-values for CCSR by the use of interpolation. FS also had previously presented a numerical procedure [6], whereby the preceding k-values could be estimated. A computer program [7] has also been reported which made it possible for the tables of FS [5] to be extended over a much larger range of values. Burkus and Eckert [8] utilized the IC and the tables of FS to calculate the k-values for a CCSR type reaction.

The aim of the present paper is to simplify the ascertainment of k-values for CCSR by means of polynomial regression analyses and a Paradox (ver. 3.5) database script. In this regard, cubic and quartic polynomials were employed (cf. Appendix A) to evaluate values of τ and Kk (to be described subsequently) which allowed the rapid calculation via computer of

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k-values for CCSR without employing special tables and interpolation.

2. Theoretical aspects

The CCSR can be represented symbolically as

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

$$\mathrm{A} + \mathrm{C} \xrightarrow{k_2} \mathrm{D} + \mathrm{E} \tag{1b}$$

where only materials A and B are present initially. The following dimensionless variables were introduced

$$\alpha = \mathrm{A}/\mathrm{A}_0,\ \beta = \mathrm{B}/\mathrm{B}_0,\ \tau = \mathrm{B}_0 k_1 t,\ Kk = 1/\kappa \tag{2}$$

where κ (kappa)$=k_2/k_1$. From Eq. (2), it can be observed that the k-values can be determined once τ (tau) and Kk have been evaluated. Thus, $k_1 = \tau/\mathrm{B}_0 t$ and $k_2 = k_1/Kk$. Further, when the IC is imposed, the following can be obtained [5]

$$\alpha = \frac{1-2\kappa}{2(1-\kappa)}\beta + \frac{1}{2(1-\kappa)}\beta^{\kappa} \tag{3}$$

$$\tau = \frac{1-\kappa}{1-2\kappa}\int_{\beta}^{1} \frac{\mathrm{d}\beta}{\beta^2[1+(1/1-2\kappa)\beta^{\kappa-1}]} \tag{4}$$

From Eqs. (3) and (4), tables could be constructed relating τ as a function of α for various κ-values and Kk as a function of time ratios. From such tables, polynomial correlations were developed in the present paper (cf. lines 13, 36 of the script in Appendix A).

3. Results and discussion

In obtaining cubic and quartic polynomial correlations, a data regression analysis was employed using Lotus 1-2-3. All the values of the square of the correlation coefficient (R^2) obtained were larger than 0.9999, with the exception of one case (0.9998+). The database script in the Appendix A employed Paradox, ver. 3.5, and runs were carried out using a 486 DX2-66 computer. From the script, it can been seen that a cubic polynomial was used initially to obtain values of Kk as a function of certain time ratios at particular percentage reaction ratios (cf. lines 16–31 of the script). From such Kk-values, τ was then determined as a function of Kk at particular values of the percentage reaction utilizing a quartic polynomial (cf. lines 38–56 of the script). From the preceding, k_1-values were calculated (see lines 40, 44, 48, 52 and 56 of the script). Lastly, final average values of k_1 and k_2 were ascertained utilizing Kk average values (see lines 63–66 of the script). These average values were displayed on the Paradox screen at the conclusion of the script run (cf. lines 70–73 of the script).

Table 1 depicts the database analysis of the rate constants for the CCSR reaction involving an ethyl adipate saponification [5]. The column names displayed in Table 1 (and Table 2) were used for the purpose of clarification. In the following are given the column names used in the tables followed by the names used in the creation of the tables in parenthesis (which were utilized in the script): Percentage reaction (PR), Time (T), Percentage compared (PC), Time ratio (TR). From the tables, it can be seen that the first column contained PR-values of 20, 30, 40, 50, 60, and 60; the respective reaction times to attain these values are listed in the second column. The preceding time values could be readily obtained from a smooth plot of conversion vs. reaction time [8]. In the construction of the tables, it was only necessary to fill in the first and second columns (the PR-values depicted in the first column must be strictly adhered to since the script only utilizes these values). All the remaining columns are automatically filled in by the script program. In the two tables, the last values in columns 5 and 7 list the average values of Kk and k_1, respectively. Due to spatial limitations of the Paradox database, the creation of an eighth column containing k_2-values was not permitted. However, as previously indicated, final average values of Kk, k_1 and k_2 are displayed on the screen at the end of the computer run.

From Table 1, final calculated average values of Kk, k_1 and k_2 are listed in the following order, each being followed by a corresponding reported value: 2.80 ± 0.03 (2.79), 0.0855 ± 0.0003 (0.0856), 0.0306 ± 0.0004 (0.0307). Table 2 data results from the database analysis of rate constants for the reaction of 2,6-tolyene diisocyanate (TDC) with 1-butanol (BuOH), which was considered to be a CCSR type reaction [8]. In the following are listed, in order, calculated average values of Kk, k_1 and k_2, each

Table 1
Database analysis of rate constants for ethyl adipate saponification

Percentage reaction	Time/s	Percentages compared	Time ratio	Kk (k_1/k_2)	τ	k_1
20	605	60/20	6.6612	2.8106	0.2582	0.08569
30	1060	60/30	3.8019	2.7962	0.4513	0.08549
40	1690	60/40	2.3846	2.7782	0.7176	0.08527
50	2595	60/50	1.5530	2.8557	1.1149	0.08627
60	4030	50/20	4.2893	2.7849	1.7140	0.08540
60	4030	50/30	2.4481	2.7516	1.7053	0.08497
				2.7962		0.08552

Table 2
Database analysis of rate constants for reaction of 2,6-TDC and 1-BuOH

Percentage reaction	Time/ min	Percentages compared	Time ratio	Kk (k_1/k_2)	τ	k_1
20	6.00	60/20	9.1167	6.1605	0.2722	0.85279
30	10.95	60/30	4.9954	6.1583	0.4970	0.85317
40	18.60	60/40	2.9409	6.0824	0.8387	0.84755
50	31.10	60/50	1.7588	6.2267	1.4194	0.85792
60	54.70	50/20	5.1833	6.1035	2.4705	0.84896
60	54.70	50/30	2.8402	6.0878	2.4672	0.84783
				6.1365		0.85137

followed by a corresponding reported value in parenthesis: 6.14 ± 0.04 (6.11), 0.851 ± 0.003 (0.852), 0.139 ± 0.0015 (0.139). From the preceding, the calculated and reported values were in excellent agreement. Further, the method employed in the present paper is very rapid and does not involve the use of special tables and interpolations therefrom. [9]

Appendix A

The Paradox script for CCSR type reactions

```
Clear Clearall
@10,1 ??"Enter molar concentration of          ;2
difunctional reactant:"
Accept "N" To B0
@12,1 ??"Enter name of table to be analyzed:"  ;4
Accept "AB" to Tabl
edit Tabl                                      ;6
moveto [PC] []="60/20" down                    ;8
[]="60/30" down []="60/40" down
[]="60/50" down []="50/20" down []="50/30"
home moveto [T] tw=[] down                     ;10
th=[] down tfo=[] down tfi=[] down
ts=[] home moveto [TR] []=ts/tw down
[]=ts/th down []=ts/tfo down
[]=ts/tfi down []=tfi/tw down []=tfi/th
;12
;——calculate Kk using a cubic equation——
;14
Scan
if [PC]="60/20" Then [Kk]=−1.880556            ;16
−0.069587*[TR]+0.1481617*[TR]*
[TR]−0.0048023*[TR]*[TR]*[TR]
endif                                          ;18
if [PC]="60/30" Then                           ;20
[Kk]=−3.596418+0.2201145*[TR]+
0.5039115*[TR]*[TR]
−0.031443 4*[TR]*[TR]*[TR]
```

```
endif
if [PC]="60/40" Then
[Kk]=-6.794938+1.082213*[TR]
+1.695887*[TR]*[TR]-0.1955*[TR]*
[TR]*[TR]
endif
if [PC]="60/50" Then
[Kk]=-2.959783-19.10309*
[TR]+21.361545*[TR]*[TR]-4.2816815*
[TR]*[TR]*[TR]
endif
if [PC]="50/20" Then
[Kk]=-7.252914+4.4139196*
[TR]-1.102495*[TR]*[TR]+0.1443217*
[TR]*[TR]*[TR]
endif
if [PC]="50/30" Then
[Kk]=-9.63089+10.13185*
[TR]-4.906499*[TR]*[TR]+1.1575954*
[TR]*[TR]*[TR]
Kkavg=caverage (Tabl, "Kk")
endif
;——calculate Tau and K1 using a
quartic equation——
if [PR]=20 Then
[Tau]=0.212966+0.026602*
[Kk]-0.004807*[Kk]*[Kk]+0.000419*
[Kk]*[Kk]*[Kk]-0.000014*[Kk]*[Kk]*
[Kk]*[Kk]
[K1]=[Tau]/(B0*[T])
endif
if [PR]=30 Then
[Tau]=0.331555+0.06749*[Kk]-0.011191*
[Kk]*[Kk]+0.0009308*[Kk]*[Kk]*
[Kk]-0.00003*[Kk]*[Kk]*[Kk]*[Kk]
[K1]=[Tau]/(B0*[T])
endif
if [PR]=40 Then
[Tau]=0.4629056+0.1359058*
[Kk]-0.019889*[Kk]*[Kk]+0.0015661*
[Kk]*[Kk]*[Kk]-0.0000493*[Kk]*[Kk]*
[Kk]*[Kk]
[K1]=[Tau]/(B0*[T])
endif
if [PR]=50 Then
[Tau]=0.6272778+0.232684*
[Kk]-0.026723*[Kk]*[Kk]+0.001929*
[Kk]*[Kk]*[Kk]-0.0000574*[Kk]*[Kk]*
[Kk]*[Kk]
[K1]=[Tau]/(B0*[T])
endif
if [PR]=60 Then
[TAU]=0.836111+0.387315*
[Kk]-0.032497*[Kk]*[Kk]+0.00259408*
[Kk]*[Kk]*[Kk]-0.0000784*[Kk]*[Kk]*
[Kk]*[Kk]
[K1]=[Tau]/(B0*[T])
endif
endscan


;——calculate final average values of
K1 and K2——


Do_It! Home
kkavg=caverage (Tabl, "Kk") kkstd=cstd
(Tabl, "Kk")
k1avg=caverage (Tabl, "k1") k1std=cstd
(Tabl, "k1")
k2md1=(k1avg+k1std)/
(kkavg-kkstd)
k2md2=(k1avg-k1std)/(kkavg+kkstd)
k2md3=(k2md1+k2md2)/2
k2std=k2md1-k2md3
editkey home end down moveto [Kk]
[]=kkavg
right right []=k1avg Do_It!
Clear @10,10
??"kkavg=", Format ("W6.2", kkavg), "+/-",
Format ("W4.2", kkstd)
@12,10 ??"k1avg=", Format ("W6.4", k1avg),
"+/-", Format ("W6.4",
k1std)k2avg=k1avg/kkavg
@14,10 ??"k2avg=", Format ("W6.4", k2avg),
"+/-", Format (W6.4", k2std)
@18,10 ??" Press <Enter> to continue."
x=getchar ()
Clearall
edit tabl
Wait Table
Prompt "Table may be edited! Press [F2]
when done."
until "F2"
Do_It!
Clearimage
```

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