Invariant Kinetic Parameters of Polymer Thermolysis. II. Butyl Rubber Pyrolysis

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Synopsis

The methodological problem of correct estimation of invariant Arrhenius parameters $\hat{A}$ and $\hat{E}$ from nonisothermal experiments has been analyzed for thermal decomposition of commercial butyl rubber in inert atmosphere. It is shown that restriction of the kinetic analysis by varying n in the function $f(\alpha) = (1 - \alpha)^n$ may yield incorrect $\hat{A}$ and $\hat{E}$. It is necessary to apply the set of $f(\alpha)$ known in the formal topochemical reactions kinetics for correct estimation of $\hat{A}$ and $\hat{E}$.

INTRODUCTION

We have shown[1] in Part I that the sequence of linear correlations ending with the correlation for the compensation effect (CE) parameters results in invariant Arrhenius parameters $\hat{A}$ and $\hat{E}$.[2-4] This invariance means independence of the experimental conditions. In particular, $\hat{A}$ and $\hat{E}$ for oxidative degradation of polyester fibers were found in Ref. 1 using the data of Ref. 5. Reasoning that $\hat{A}$ and $\hat{E}$ can be used along with the compensation parameter $\hat{T}_i$ to estimate the effective decomposition rate constants during combustion for polymers containing fire retarders have been given in the same work. This outlines possible practical applications of invariant kinetic parameters. As an example, we have analyzed in this paper is a methodologically important problem of correct estimation of invariant Arrhenius parameters for the thermal decomposition of commercial butyl rubber (BR). The numerical data of these parameters were reported earlier.[6]

$\hat{A}$ and $\hat{E}$ can be found by varying temperature and another two variables.[7] In a nonisothermal kinetic approach, those may be[2] the kinetic function $f(\alpha)$, which variation as usual will hardly affect the statistical indices of the linearized form of the basic nonisothermal kinetic equation

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) f(\alpha) \tag{1}$$

and the linear heating rate β.

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A variation of $f(\alpha)$ results in the apparent CE

$$\log A = \log \hat{k}_i + \frac{E}{2.3R\hat{T}_i} \qquad (2)$$

yielding $\log \hat{k}_i$ and $\hat{T}_i$ for each heating rate β_i, while a variation of β_i results in the correlation of the Arrhenius equation type

$$\log \hat{k}_i = \log \hat{A} - \frac{\hat{E}}{2.3R\hat{T}_i} \qquad (3)$$

yielding $\log \hat{A}$ and $\hat{E}$.

The kinetic function $f(\alpha)$ corresponding to $\hat{A}$ and $\hat{E}$ can be found[8] by minimizing the sum of squares of deviations of experimental $d\alpha/dT$ from the same terms calculated upon substituting $\hat{A}$ and $\hat{E}$ in eq. (1). The errors in $\hat{A}$ and $\hat{E}$ hamper the exact estimation of $\hat{f}(\alpha)$; therefore, we can only speak of a most probable function $\hat{f}(\alpha)$.

The formal kinetics of polymer thermolysis[9] usually uses $f(\alpha)$ in the form of

$$f(\alpha) = (1 - \alpha)^n \qquad (4)$$

In this case, however, an uncertainty in choosing the formal reaction order n arises. For some limits of n, it cannot be resolved with the aid of traditional statistical analysis.[10] The errors in the estimation of n give errors in the values of A and E, which make it impossible to use A and E to calculate the rate constant by extrapolation to another temperature range. Note that the kinetic function $f(\alpha)$, used to describe polymer pyrolysis in the form of eq. (4) or any other form known for topochemical reactions is formal, i.e., it does not give an explicit description of the process mechanism.

If an exact expression be found for $f(\alpha)$, then A and E calculated with this function would be identical to $\hat{A}$ and $\hat{E}$.[8] However, because of an uncertainty of choice of $f(\alpha)$, it is more appropriate to estimate the Arrhenius parameters with the algorithms not connected with a preliminary estimation of $f(\alpha)$, in particular, by varying this function, as mentioned above. It is shown in this paper that restriction of $f(\alpha)$ variation exclusively to the variation of n in eq. (4) may result in erroneous $\hat{A}$ and $\hat{E}$.

RESULTS AND DISCUSSION

The thermal decomposition of commercial sample of butyl rubber having composition $C_{71.296}H_{142.592}$ and molecular weight 29000 ± 1000 a.u. was studied. Complex thermal analysis using derivatograph of Hungarian firm MOM of the F. Paulik, J. Paulik, and L. Erdey[11] system was carried out. The decomposition of 100, 70, and 40 mg samples was performed in platinum holders in inert argon atmosphere (gas flow was about 5 L/h). The linear heating rate was ranged from 1 to 21°/min. The derivatograph was calibrated against temperature utilizing standards of $KClO_4$, KNO_3, and Ag_2SO_4.
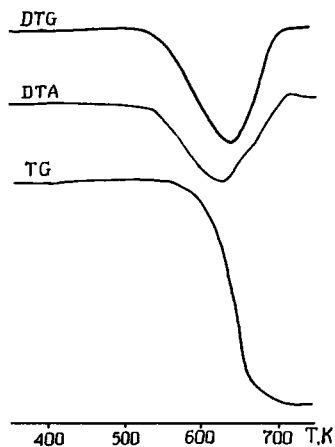
Fig. 1. DTA, DTG, and TG curves for butyl rubber thermal decomposition. Heating rate 5°C/min.

BR broke down within the 570–670 K range in inert atmosphere. Only one endothermal peak was observed (Fig. 1). Changing the sample weight or heating rate did not affect the kinetics of process, but, as the heating rate increased, the weight loss proceeded at higher temperature (Fig. 2). Hence, we use only experimental data for the 100 mg sample weight in our further discussion.

The Arrhenius parameters were calculated by the mass loss curve. Degree of decomposition within the $0 < \alpha < 0.8$ range was used to prevent the complication and misrepresentation of kinetics due to the accumulation and resinification of the BR decomposition products. Sensitivity of derivatograph made it possible to obtain no less than 30–40 reliable experimental points within this α range. The effective Arrhenius parameters were calculated using the Coats–Redfern method.[12] In one case, $f(\alpha)$ was used in the form of eq. (4), with the power exponent n ranging from 0.5 to 2.0, so that, in the vicinity of $n = 1$, the increments were less than around $n = 0.5$ and $n = 2.0$. On the whole, 20 different gradations of n were scanned. In the other case, the form
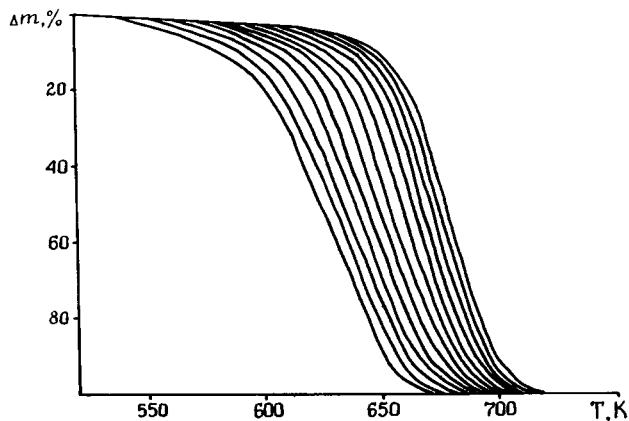

Fig. 2. Weight loss curves for butyl rubber thermolysis. Heating rates (from left to right) correspond to those in Table I.

TABLE I

Boundary Values of the Arrhenius Parameters and CE Parameters for Butyl Rubber Thermolysis Obtained for Variable $f(\alpha)$ Form and n in Eq. (4)

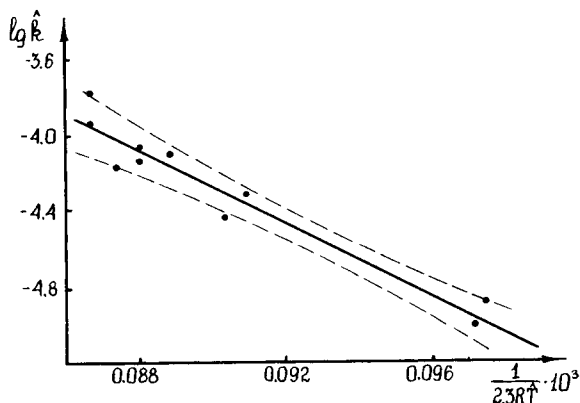| | Variable | | | | | | | | | | | |
| | $f(\alpha)$ Form | | | | | | n in Equation $f(\alpha) = (1 - \alpha)^n$ | | | | | |
Heating rate	E_{max}	$\log A_{max}$	E_{min}	$\log A_{min}$	$\log \hat{k}$	$\frac{1}{2.3R\hat{T}} \times 10^3$	E_{max}	$\log A_{max}$	E_{min}	$\log A_{min}$	$\log \hat{k}$	$\frac{1}{2.3R\hat{T}} \times 10^3$
1.0	192.4	11.74	13.7	-3.10	-3.744	0.0817	110.4	5.90	94.3	3.89	-5.004	0.0985
1.1	280.9	19.11	23.6	-2.02	-3.501	0.0812	162.0	10.28	132.5	7.53	-4.827	0.0931
1.25	271.4	18.49	22.3	-2.08	-3.461	0.0816	158.5	10.12	127.7	7.23	-4.752	0.0937
2.39	355.2	24.77	32.5	-0.91	-3.060	0.0769	201.1	13.44	170.4	10.65	-4.573	0.0892
2.7	347.7	24.13	30.8	-1.02	-3.030	0.0786	205.8	13.86	166.3	10.33	-4.511	0.0890
3.2	276.6	18.42	22.9	-1.71	-3.674	0.0785	158.7	10.00	130.7	7.45	-4.444	0.0908
3.6	163.7	8.74	11.0	-2.99	-3.332	0.0755	87.7	3.82	75.2	2.59	-4.867	0.0989
4.65	341.0	23.52	30.1	-0.90	-2.814	0.0779	198.0	13.23	162.5	10.10	-4.137	0.0874
5.0	362.9	25.66	32.8	-0.57	-2.738	0.0788	209.6	14.40	173.3	11.19	-4.135	0.0822
6.6	331.8	23.21	28.9	-0.82	-2.699	0.0785	188.1	12.71	157.8	9.98	-4.095	0.0891
8.5	233.9	14.63	18.6	-1.81	-2.764	0.0755	130.6	7.67	111.3	5.90	-4.303	0.0914
11.8	312.9	21.07	27.8	-0.77	-2.462	0.0760	180.0	11.85	148.6	9.16	-4.052	0.0882
12.5	333.5	22.62	29.4	-0.61	-2.417	0.0757	190.6	12.60	158.8	9.88	-3.929	0.0867
15.4	264.1	17.30	21.3	-1.29	-2.451	0.0756	61.2	1.92	53.1	1.08	-4.450	0.1038
16.7	355.0	24.66	32.1	-0.22	-2.247	0.0764	200.8	13.69	168.3	10.87	-3.758	0.0867
21.0	334.0	23.11	28.7	-0.43	-2.195	0.0763	74.8	3.28	62.8	2.09	-4.150	0.0933

Fig. 3. Linear correlation between CE parameters obtained for variable n.

of the kinetic function $f(\alpha)$ was varied. Here 20 functions usually used in formal kinetics of chemical reactions and cited in Ref. 13 were tested at each heating rate. The computations were performed on a microcomputer.

It is worth noting that both with variable n and $f(\alpha)$ the known statistical criteria (correlation index, standard error) changed insignificantly and that did not allow us to choose certain $f(\alpha)$ or n. The Arrhenius parameters log A and E, which boundary values are given in Table I, are seen to vary appreciably. In such a situation the solution of the inverse kinetic problem has greater uncertainty. To be particular, the ambiguity of the Arrhenius parameter with variable $f(\alpha)$ is $E = 11 \div 363$ kJ mol^{-1}, $\log(A/s^{-1}) = -3 \div 26$; for varying n, $E = 53 \div 210$ kJ mol^{-1}, $\log(A/s^{-1}) = 2 \div 14$.

It can be easily seen from Table I that the uncertainty in E and log A at a fixed heating rate with n ranging from 0.5 to 2.0 is somewhat less than it is in case when 20 different $f(\alpha)$ are substituted into eq. (1), but it is still great in the former case. As was already noticed,[14,15] such uncertainty results in the apparent CE. In the case under consideration at a fixed heating rate the calculated E and log A correlate in all cases, and the correlation indices are not less than 0.999. The CE parameters log $\hat{k}$ and $1/2.3R\hat{T}$ from eq. (2) are also presented in Table I. In general, it is seen that log $\hat{k}$ and $1/2.3R\hat{T}$ are varying in opposing manner if heating rates are varied. There is a linear dependence of type (3) between them (Fig. 3). The dependence is plotted here for the case when the heating rate and n are variables. The case of variable $f(\alpha)$ is considered in Ref. 6. Such examples omit six heating rates out of 16. Corresponding points are discarded in accordance with statistical criteria. The calculated invariant kinetic parameters are for variable $f(\alpha)$, $\hat{E} = 195 \pm 25$ kJ mol^{-1} and $\log(\hat{A}/s^{-1}) = 12 \pm 2$; for variable n, $\hat{E} = 85 \pm 20$ kJ mol^{-1}, $\log(\hat{A}/s^{-1}) = 5 \pm 1.5$. We shall analyze possible reasons for the difference in the kinetic parameters calculations.

The pencil formed by straight lines (2) intersecting in a small common area is the reason for the existence of the linear relations of type (3). Figures 4 and 5 illustrate the straight lines the parameters of which were given in Table I. Their lengths are restricted by the points for E_{min}, log A_{min} and E_{max}, log A_{max} in Table I. The dashed curve represents the residual sum of squares of deviation of the lines from the center line calculated by the method
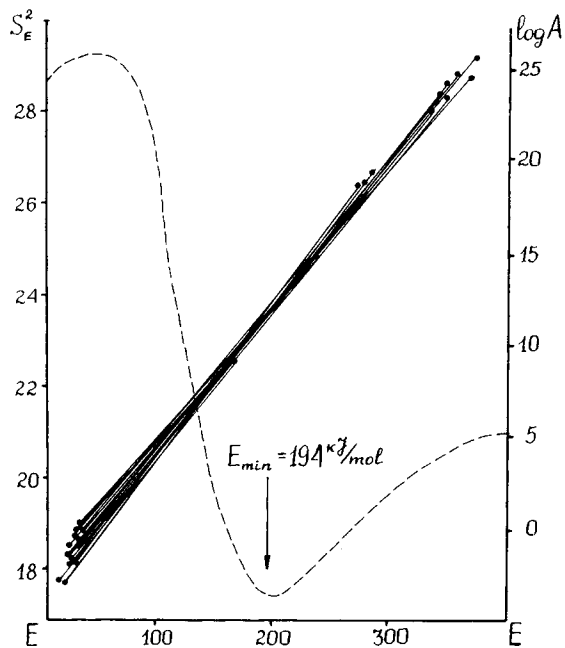
Fig. 4. Pencil of straight lines of the CE obtained for variable $f(\alpha)$ form. The line length is restricted by the points corresponding to E_{min}, $\log A_{min}$, and E_{max}, $\log A_{max}$ (Table I). Dashed curve is residual sum of squares calculated by means of the Exner method.[17]
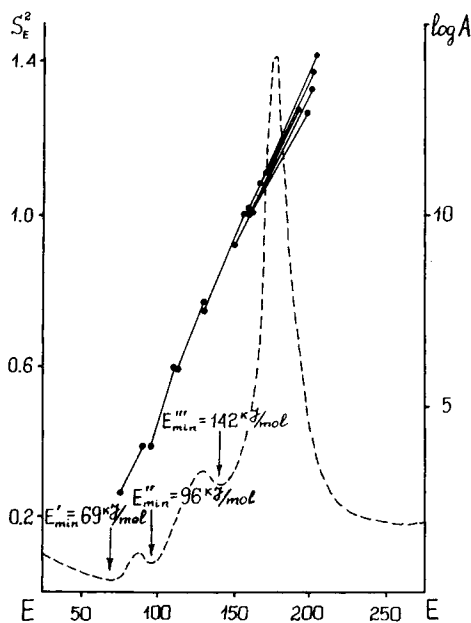

Fig. 5. Compensation effect lines of different heating rates at variable n in eq. (4). For notations see Figure 4.

suggested in Ref. 16. The closest convergence and intersection of the lines, i.e., the pencil center corresponds to the curve minimum.

It can be seen from Figure 4 that for the case of variable $f(\alpha)$ the minimum is at 195 kJ mol^{-1}. The latter coincides with the above-mentioned value of $\hat{E}$. Minimization of the sum of squares of experimental $d\alpha/dT$ deviations from the same values calculated for eq. (1) with substituted $\hat{E}$ and $\hat{A}$ marks out $\hat{f}(\alpha) = [(1 - \alpha)/n][-\ln(1 - \alpha)]^{1-n}$ with the power exponent $n = 1/3$ as the most probable function. The situation in Figure 5 is different. The straight lines don't have a common intersection point. There are three minima on the curve $S^2 = f(E)$ at $E' = 69$ kJ mol^{-1}, $E'' = 96$ kJ mol^{-1}, and $E''' = 142$ kJ mol^{-1}. It is worth noting that none of the above values coincides with $\hat{E} = 85$ kJ mol^{-1} obtained from linear relationship (3). Since E and $\log A$ don't change so significantly at variation n within $0.5 + 2.0$, then at $f(\alpha)$ variation the calculation of the intersection point is likely to involve certain errors due to the extrapolation of short sections.[17] Besides, the occurrence of local minima may be attributed to a change in the calculated mean E,[18] i.e., the lines noticeably shift along E as the heating rate changes.

So, if $f(\alpha)$ is one of the variables in the estimation of invariant kinetic parameters, then the restriction of variation by changing n in eq. (4) alone will not give correct $\hat{A}$ and $\hat{E}$. In order to obtain correct $\hat{A}$ and $\hat{E}$ values, it is mandatory to vary the form of the function $f(\alpha)$. The experience gained in finding $\hat{A}$ and $\hat{E}$ shows that, in this case, the $f(\alpha)$ set usually used in formal kinetics of topochemical reactions may be appropriate.

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