Invariant Kinetic Parameters of Polybutadiene Binders Thermal Decomposition

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Introduction

THERMAL decomposition of a series of polybutadiene binders was investigated in Ref. 1. The kinetic parameters E and A in the Arrhenius equation have been determined by dynamic thermogravimetry for seven heating rates (1-100 deg/min^{-1}) using three different integral equations. Different values of E (82-156.5 kJ·mol^{-1}) and $A(3.85 \cdot 10^3 - 1.41 \cdot 10^8 \mathrm{s}^{-1})$ have been obtained in each separate experiment. The mean values of E and A were found to be close for all the binders ($<E> = 110$ kJ·mol^{-1} and $<A> = 10^5 \mathrm{s}^{-1}$). Since many methods have been developed for analyzing the nonisothermal kinetic data, and different functions $g(\alpha)$ can describe the experimental results, selective application of several calculation methods and functions $g(\alpha)$ to find the mean values of E and A does not constitute grounds for preferring these data.

In a recent Note, Price[2] reported that the results of Ref. 1 were unacceptable for propellant combustion because of the dependence of E on the heating rate and the higher temperature on the burning surface. Indeed, in nonisothermal kinetics, the apparent dependence of kinetic parameters on the heating rate and the method of calculation is well known and has been confirmed more than once.[3-5] Moreover, variations of the kinetic function $g(\alpha)$ also change E and A significantly.[5] In such cases we are dealing with a kinetic compensation effect (CE) which is a computational artifact.[6] Therefore, the above dependence may also be an artifact.

In Refs. 7 and 8 a method for estimating invariant effective $\hat{E}$ and $\hat{A}$ values, which are independent of the calculation method and the heating rate if such a dependence is an artifact, is presented. The method allows elimination of the compensation effect by finding the intersection point of the Arrhenius sketch lines corresponding to E and A calculated by various methods and related by

$$\log A = B + eE \tag{1}$$

The latter is the mathematical condition of the formation of these lines, each corresponding values $B = \log k_i$ and $e = 1/2.3RT_i$, which are coordinates of the ith point of intersection (k is the rate constant; T the temperature; R the gas constant). A change in the heating rate causes B and e to vary (in agreement with the Arrhenius equation), which makes it possible to find invariant $\hat{E}$ and $\hat{A}$. The applicability of the method in question to varying $g(\alpha)$ is discussed in Ref. 8 and, in a recent paper[9], it is shown that this method improves the conditionality of the inverse kinetic problem. We shall show the validity of the method when E and A are found using various integral equations. However, the most important finding of this note is a considerable difference in the mean ($<E>$, $<A>$) and invariant ($\hat{E}$, $\hat{A}$) values of E and A discussed in connection with the use of kinetic parameters in combustion models.

We have made use of ample kinetic data[1] and calculated the parameters of relation (1) (42 relations altogether) for every heating rate and size of the charge. These relations are valid when the correlation factor is greater than 0.999 (0.877 being the only exception). Such high correlation factors are evidence that the compensation effect is a computational artifact, as they are usually lower[10] in real compensation relations. The values of B and e yielded straight lines with more or less satisfactory statistical indices. Fig. 1 shows B vs e for the HTS binder and indicates an error "corridor." In Fig. 2, lines (1) corresponding to this dependence are given. Note that actual statistical indices should be found, taking into account the primary measurement errors missing in Ref. 1, so the abovementioned indices characterize (in a limited measure) the validity of the linear dependence of B on e. Probably the increase of the number of heating rates in their range, or the increase of the range itself, would improve the statistical indices of B vs e (provided the kinetics parameters are constant for this domain). The values of $\hat{E}$ and $\hat{A}$ for all the binders are presented in Table 1.

Use of the data from the experiments with varying charges (Table 7 in Ref. 1) yielded large errors in determning $\hat{A}$ and $\hat{E}$ from the dependence of B on e, which indicates that it is inadvisable that $\hat{A}$ and $\hat{E}$ be found from the results of such experiments. In this case the sample size shifts the thermoanalytical curve slightly along the temperature axis, with the result that B and e change insignificantly.

The experimental data confirm the conclusion[1] about approximate equality of kinetic parameters for all the binders (Table 1); however, $\hat{A}$, $\hat{E}$, and the mean values of invariant A and E (i.e., 5£A⅝ and $<\hat{E}>$) differ greatly from the values of A and E found in Ref. 1 and from $<A>$ and $<E>$ as well. It is noteworthy that the values of $\hat{A}$ are close to the normal values of the pre-exponential factor (10^{14} s^{-1}) considered

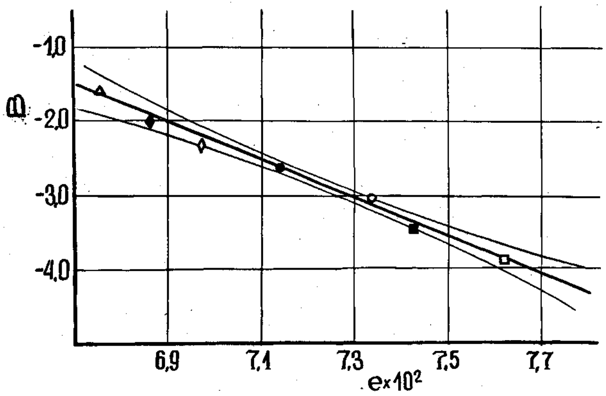

Fig. 1 B vs e for the HTS with an error "corridor."

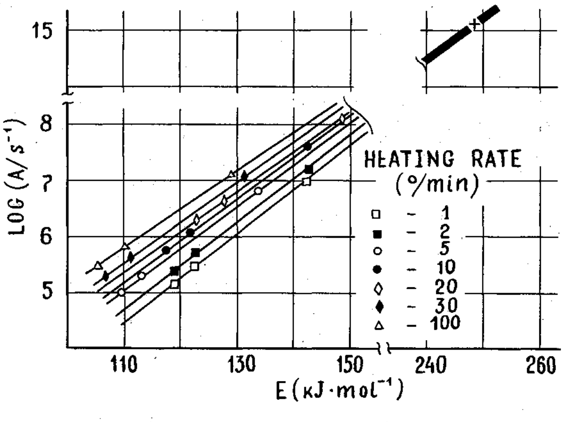

Fig. 2 Compensation sketch for the HTS binder with + the predicted point of intersection.

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Table 1 Invariant values of log A and E and calculated rate constants for the binders in Ref. 1

Code	$\log(\hat{A}/s^{-1})$	$\hat{E}(\mathrm{kJ \cdot mol^{-1}})$	$\log(k_{750}/\mathrm{s}^{-1})$	$\log(k_{1000}/\mathrm{s}^{-1})$
ISRO-CTPB	17.65	283.5	−2.10	2.84
HC-434	16.76	270.8	−2.11	2.61
CTL	16.24	264.8	−2.21	2.40
ISO-HTPB	15.96	262.1	−2.30	2.26
HTS	15.09	248.6	−2.23	2.10

to be the frequency factor during a homolytical break of the chemical bond. As to the $\hat{E}$ values, the available data[3,11,12] give very diverse values for E for carbon-chain polymers (from about 85 to 325 $\mathrm{kJ \cdot mol^{-1}}$, sometimes more[13]). This may be due not only (but perhaps slightly) to different chemical natures of polymers, but also to the effect on A and E on the thermolysis conditions and the behavior of the compensation effect as a computational artifact. The value of $<\hat{E}>$ we found is close to the energy of the C—C bound weakened by the adjacent allyl fragment (250-310 $\mathrm{kJ \cdot mol^{-1}}$).[14] We may assume that during pyrolysis of many carbon-chain polymers, decomposition is limited by a homolytical break of the weakest C—C bond and, therefore the pyrolysis activation energy is equal to the energy of these bonds. Within this assumption, the values of $\hat{E}$ are in accord with the normal value of the frequency factor $\hat{A}$.

Besides the theoretical aspect (that is, finding of a relationship between E, A, and a process mechanism), there is another aspect of the problem under consideration; namely, extrapolation of the measurement results at comparatively low temperatures to the combustion surface temperatures of the system wherein the above binders are used. In the theoretical combustion models, E and A are part of the Arrhenius expression for the rate constant k. When a compensation effect is due to computational effects, broad variations of E and A within Eq. (1) do not give rise to considerable changes in k at temperatures where the rates were measured. The values of log k for 750 K in Table 1 suggest this statement. These values agree with the corresponding values of log k calculated from the data in Ref. 1, the mean value of $\log <k_{750}> = -2.18$ from Table 1 is close to the one (-2.7) Ref. 1 from at $<E> = 110$, $\log <A> = 5$. However, during extrapolation to a temperature that corresponds approximately to the solid propellant combustion temperature (1000 K[15], the real temperature on the polymer surface as such is unknown), these values of $<E>$ and $\log \underset{\smile}{<A>}$ lead to $\log <k_{1000}> \approx -0.7$, while the use of $\hat{E}$ and $\hat{A}$ from Table 1 yields $\log <k_{1000}> \approx 2.5$; that is, a constant that is almost three orders of magnitude higher than the previous one. The differences in the values of k seem to be due to the fact that compensation of A and E variations according to Eq. (1) does not change k only at a definite T.

The value of $\log <k_{1000}> = -0.7$ is too small for 1000 K; it corresponds to the half-reaction time in the first-order reaction $t_{1/2} \approx 3.5$ s. A rough estimate of half of the residence time for the substance in a 10^{-2} cm thick reaction layer at a 0.5 $\mathrm{cm \cdot s^{-1}}$ propellant combustion rate yields 10^{-2} s (according to Ref. 16 reaction time in a condensed phase is 10^{-3} s). We found this time to be close to $t_{1/2} \approx 0.2\ 10^{-2}$ s for $\log <k_{1000}> \approx 2.5$.

Thus the invariant effective kinetic parameters, calculated by the suggested method, allow one to obtain a realistic assessment of the rate constant of the polybutadiene binder decomposition both at combustion and model experiment temperatures, and can be used for extrapolations. However, the possibility of such an extrapolation for some other substance needs special consideration. The method is based on traditional experimental and data processing technique, and the use of a microcomputer helps to cope with a somewhat bigger volume of computation. In general, the main restrictions of the method are attributed to the assumption on the validity of the unique Arrhenius law in the experimental temperature and rate ranges that are not always satisfactory. In case of the true but not apparent dependence of the kinetic parameters on T and the heating rate, both in our method and many other approaches, it is not easy to reliably isolate it statistically from the random errors.

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