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THERMOLYSIS OF POTASSIUM TETRAPEROXOCHROMATE(V) IV. EFFECT OF ADDITIVES ON ORDINARY AND SELF-PROPAGATING DECOMPOSITION

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ABSTRACT

The dependence of the rate of self-propagating high-temperature decomposition (SHD) on several variable factors may be approximated by a polylinear function. The applicability and predictability of the polylinear expansion of the rate of K_3CrO_8 SHD as a function of external pressure and activity of additives are shown. The limits of the K_3CrO_8 SHD rate regulation due to additives are specified. Invariant values of the kinetic parameters of decomposition of the mixtures based on K_3CrO_8 are estimated. The mechanism of the effect of different additives on K_3CrO_8 SHD is discussed.

INTRODUCTION

The study of various aspects of the thermolysis of potassium tetraoxochromate(V) (K_3CrO_8) [1–3] enabled the understanding of the mechanism of ordinary thermolysis of this substance and the building of a physical model of self-propagating high-temperature decomposition (SHD). However, the estimation of the SHD rate using elementary physical models [3] gave inaccurate values for the rate due to the uncertainties in kinetic parameters. In fact, the order of magnitude of the SHD rate can only be estimated. The SHD rate and its dependence on the process conditions may be estimated more exactly using the known experimental and statistical methods [4]. The latter distinctly show how strongly the response function is affected by variable parameters. The reasons for this effect are not explained, however. The combination of physical and experimental–statistical modelling would allow one to make use of the advantages of both modelling methods and to smooth their shortcomings. However, it is hindered by a diversity of concrete expressions (ordinary polynomial) for the response function which are objectively chosen based on statistical criteria. This difficulty may be eliminated partly by chosing a universal polynomial representation of the response function and considering only the cases for which it is valid.

In the paper, the applicability of the polylinear representation of the SHD rate dependence on the external inert gas pressure and nature of additives is shown for the SHD of K_3CrO_8. The feasibility of isoparametric relations is considered as a simple criterion of polylinear representation applicability.

POLYLINEAR FUNCTION APPROXIMATION METHOD

As a general approximation in physico-organic chemistry [5], the polynomial part of the function expansion of n arguments of x (on which depends the system property under review) is given by

$$f(x_1, x_2, \ldots x_i, \ldots x_n) = f(x_1^0, x_2^0, \ldots x_i^0, \ldots x_n^0) + \sum_{i=1}^{n} a_i x_i' + \gamma \sum_{i=1}^{n} \sum_{j=1}^{n} a_i a_j x_i' x_j' + \ldots + \gamma^{n-1} \prod_{i=1}^{n} a_i x_i' \tag{1}$$

In the homogeneous polylinear function (1), x_i' are the parameters dependent only on the arguments x_i; x_i^0 are the standard values of the arguments; a_i are the scale factors and γ is a constant. Transformation of eqn. (1) to the form

$$f(x_i) = f(x_i^0) - \gamma^{-1} + \gamma^{-1} \prod_{i=1}^{n} (1 + \gamma a_i x_i') \tag{2}$$

shows that this function possesses an isoparametric property, i.e., it no longer depends on every value of x_i' if any of the x_i' arguments become $\hat{x}_i' = -\dfrac{1}{\gamma a_i}$ ($\hat{}$ stands for isoparametric value)—called an isoparametric point for the parameter x_i'. The applicability of the polynomial approximation may be indicated by the validity of isoparametric relationships which, in particular, include the correlation

$$\log \beta = a - b\nu \tag{3}$$

between the parameters β and ν entering the power-law dependence of the SHD (U) on pressure (p)

$$U = \beta p^{\nu} \tag{4}$$

The validity of eqn. (3) for different heterogeneous mixtures is discussed in ref. 6. Let us consider the most simple two-parametric version of function (1), namely

$$f(x_1, x_2) = f(x_1^0, x_2^0) + a_1 x_1' + a_2 x_2' + \gamma a_1 a_2 x_1' x_2' \tag{5}$$

For the case of U vs. p and activity (κ) introduced into the mixture additive, the polynomial of type (5) presented earlier [7,8] may be obtained from eqns. (3) and (4) as follows. From eqn. (4) we find $\log U_{p^0}$ at $p = p^0$ chosen as standard. Substituting the expression found into eqn. (3) we obtain $\nu = \dfrac{a + \log U_{p^0}}{b - \log p^0}$. Expressing a from eqns. (3) and (4) for the system chosen to be standard (indicated by ^{0}) at $p = p^0$: $\log U^0_{p^0} = \log \beta^0 + \nu^0 \log p^0 = a - b\nu^0 + \nu^0 \log p^0$, $a = \nu^0(b - \log p^0) + \log U^0_{p^0}$ and substituting into the expression of ν we get $\nu = \nu^0 - \dfrac{\log U_{p^0} - \log U^0_{p^0}}{b - \log p^0} = \nu^0 - \dfrac{\kappa}{b - \log p^0}$, where $\kappa = \log\dfrac{U_{p^0}}{U^0_{p^0}}$. Substituting the expression obtained for ν into the equation derived from eqns. (3) and (4) for an arbitrary case, i.e., into $\log U = a - b\nu + \nu \log p$, and we obtain

$$\log U = \log \beta^0 + \nu^0 \log p + \frac{b}{b - \log p^0}\kappa + \frac{1}{\log p^0 - b}\kappa \log p \tag{6}$$

Comparing the above with eqn. (5) shows $\log \beta^0 = f(x^0_1, x^0_2)$; $\nu^0 = a_1$; $\log p = x'_1$; $\kappa = \log\dfrac{U_{p^0}}{U^0_{p^0}} = x'_2$; $\dfrac{b}{b - \log p^0} = a_2$; $-\dfrac{1}{\nu^0 b} = \gamma$.

An alternative equivalent form of eqn. (6) may be obtained by using eqn. (5) where the isoparametric value of the variable x'_1 is represented by $\hat{x}'_1 = \mathrm{b} = \log \hat{p} = -\dfrac{1}{\gamma a_1}$, so $a_1 = -\dfrac{1}{\gamma b} = \nu^0$. Similarly $\hat{x}'_2 = \hat{\kappa} = -\dfrac{1}{\gamma a_2}$, so $a_2 = -\dfrac{1}{\gamma\hat{\kappa}} = \dfrac{\nu^0 b}{\hat{\kappa}}$. So, eqn. (5) assumes the form

$$\log U = \log \beta^0 + \nu^0 \log p + \frac{\nu^0 b}{\hat{\kappa}}\kappa - \frac{\nu^0}{\hat{\kappa}}\kappa \log p \tag{7}$$

Here $\hat{\kappa} = \nu^0(b - \log p^0) = a - \log U^0_{p^0} = \log\dfrac{\hat{U}}{U^0_{p^0}}$, i.e., the value of $\hat{\kappa}$ is sought from eqn. (3). This value may also be found from the isoparametric relation

$$\log U_{\kappa=0} = a - \hat{\kappa}c \tag{8}$$

which is similar to eqn. (3) and where $\log U_{\kappa=0}$ and c are the parameters of the linear dependence

$$\log U = c\kappa + \log U_{\kappa=0} \tag{9}$$

obtained from experimental data at various values of p. It is appropriate to represent polynomial (7) as

$$\log U = a - b\nu^0\left(1 - \frac{\log p}{b}\right)\left(1 - \frac{\kappa}{\hat{\kappa}}\right) \tag{10}$$

As the isoparametric values $a = \log \hat{U}$ and $\hat{\kappa}$ are the coordinates of the point of intersection of lines (9) and $a = \log \hat{U}$ and $\log \hat{p}$ of linearized curves (4), then the parameters of polynomial (10) may be estimated using the statistical technique of specifying the centre of the pencil of lines (some of the lines with a common point of intersection) [9]. It is evident that parameters of polynomials (6), (7) and (10) may be obtained using the ordinary regression analysis, i.e., if eqn. (3) is fulfilled then from eqn. (4) leads to eqn. (6), i.e., to the partial case of eqn. (1).

EXPERIMENTAL

The experimental study of thermolysis in non-isothermal conditions was made as in ref. 2 and of SHD as in ref. 3.

The SHD of K_3CrO_8 with additives (< 50 μm) of substances of different chemical nature (fluoroplastic, polymethylmethacrylate (PMMC), rosin, ferricenium reinekate, i.e., bis-cyclopentadienylferrum(III)tetrathiocianato-*N*-diaminochromate(III) of the formula $[(C_5H_5)_2Fe][Cr(NCS)_4(NH_3)_2]$, zinc oxide). These additives were chosen taking account of the data on their efficiency and use in combustible mixtures [10,11]. Five weight % of additives were introduced and thoroughly mixed with K_3CrO_8. The parameters ν and β were calculated using the linearized form of eqn. (4) following the regression analysis. All the experimental data satisfy the conditions of the hypothesis on the homogeneity of dispersions of reproducible and linear functions at 95% significance level.

Similarly, the results were treated in coordinates of other linear relationships, in particular, to determine the Arrhenius parameters A and E by the earlier method [2]. These procedures, as well as the calculations by the method of Exner [9] for determining the coordinates of isoparametric points, were performed on a micro-computer.

RESULTS AND DISCUSSION

Invariant values of the activation parameters were estimated from the Arrhenius dependences for isoparametric values of the rate constant logarithms vs. inverse temperature obtained from the results for the decomposition of pure potassium tetraperoxochromate and its mixtures at some heating rates (from 0.6 to 20°C min^{-1}). For pure K_3CrO_8 and mixtures with added fluoroplastic, zinc oxide and rosin, their mean values are, respectively: $E = 60.7$, 51.9, 56.5 and 69.0 kJ mol^{-1}; $\log A = 6$, 5, 5.5 and 7 s^{-1}.

Rosin, ferricenium reinekate and polymethylmethacrylate in the pressure range studied (1–10 MPa) behaved as SHD accelerators (Table 1). These additives are characterized by low values of ν (0.1–0.25) and relatively high values of $\log \beta$ (1.4–1.6). The accelerating effect of these additives is, presumably, due to their oxidation by the products of K_3CrO_8 thermolysis. This oxidation makes an extra exothermic contribution to the condensed phase.

TABLE 1

Experimental and calculated [a] propagation rates of potassium tetraperoxochromate(V) thermolysis ($a = 1.83$, $b = 1.76$ mm s^{-1})

Pressure (MPa)		Additives (5%), κ and law (4)					
		Without additives $\kappa = 0$ $\log U = 1.46 + 0.18 \log p$	Fluoroplastic $\kappa = -0.24$ $\log U = 1.08 + 0.46 \log p$	ZnO $\kappa = -0.10$ $\log U = 1.30 + 0.30 \log p$	Ferricenium reinekate $\kappa = 0.18$ $\log U = 1.62 + 0.16 \log p$	Rosin $\kappa = 0.16$ $\log U = 1.68 + 0.10 \log p$	PMMC $\kappa = 0.22$ $\log U = 1.62 + 0.25 \log p$
2.03	Exp.	33	17	25	45	51	49.5
	Calc.	33.8	18.1	26.0	54.4	51.3	61.0
4.05	Exp.	37	21	29	56.5	53	61
	Calc.	39.0	23.8	31.6	57.0	54.3	62.4
6.08	Exp.	41	29.5	35	60	60	66
	Calc.	42.6	28.1	35.6	58.8	56.3	63.5
8.10	Exp.	42	30	39	55	58	69.5
	Calc.	45.2	31.4	38.7	60.0	57.6	64.1
9.12	Exp.	43	33	38	58	57	64
	Calc.	46.3	33.0	40.1	60.5	58.2	64.4

[a] See eqn. (11) in text.

Fluoroplastic and zinc oxide hamper the process by acting as inert solvents and additional sources of heat release. They are characterized by high values of ν (0.3–0.5) and relatively low values of log β (0.6–1.0).

It should be noted that because of only moderate accuracy of temperature profile measurements [3] we failed to observe the changes in surface temperature both with the addition of SHD activators and with inhibitors. Neither of the above values of log A and E show appreciable changes in the kinetic parameters of ordinary K_3CrO_8 thermolysis with some additives. However, in the SHD regime the situation with the additive effect on K_3CrO_8 decomposition kinetics may change sharply. Indeed, ordinary K_3CrO_8 decomposition proceeds at rather low temperatures when chemically active additives do not yet react with the products of K_3CrO_8 thermolysis while inert additives, because of slow process, essentially do not change heat transfer conditions. In the case of SHD, temperature and time regimes change appreciably. Inert additives deteriorate heat transfer and reduce the degree of decomposition (α_s) in the leading zone of SHD. This results in the increase of the degree of K_3CrO_8 dispersion into a liquid layer of SHD products [3] and, hence, in a stronger dependence of the process rate on pressure. A similar effect of active additives is balanced and even increased by an opposite effect, which is their rapid oxidation at high temperatures leading to α_s increase, i.e., ν decrease.

For mixtures based on K_3CrO_8, the correlation for log β and ν holds (Fig. 1). The deviation is only observed for the point corresponding to the mixture with polymethylmethacrylate—characterized by a greater ν compared with other activators. For this mixture with an easily evolved monomer at ≈ 523 K [12] interaction of the gas with oxygen and so resulting in a gas flame may be expected to contribute to the SHD rate. So, some increase in ν and deviation from the common curve (Fig. 1) for this mixture are attributed to the superposition of the gas-phase combustion mechanism. On

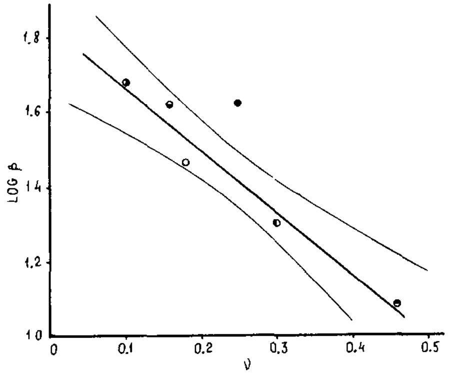

Fig. 1. Evaluation of the isoparametric log β vs. ν curve for K_3CrO_8 with various SHD regulators ($p = 0.1$–10 MPa).

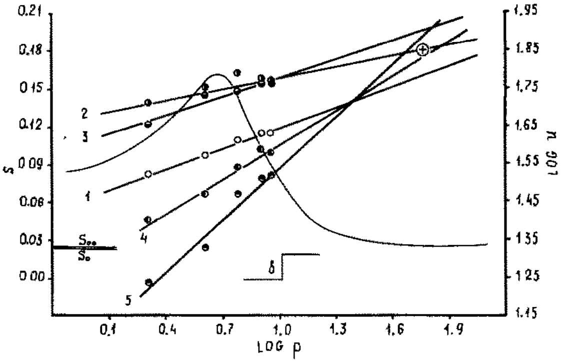

Fig. 2. Finding the coordinates of the isoparametric point following Exner's method for K_3CrO_3-based mixtures: (1) no additive; (2) rosin; (3) ferricenium reinekate; (4) zinc oxide; (5) fluoroplastic.

the whole, the validity of eqn. (3) for K_3CrO_8 agrees with the viewpoint developed in ref. 1 on the unique nature of the combustion mechanism within the correlation series and its change for mixtures which do not obey eqn. (3). The results also show that in the general case the variation of ν and β cannot be only related to the changing contribution of chemical reactions in the gas phase to combustion. The effect of generated gas on $U(p)$ may also be of purely physical nature.

Figure 2 represents the results of the application of the method of Exner [9] to find the coordinates of the isoparametric pressure point for the K_3CrO_8 mixtures (except for the mixture with PMMC). They proved to be $a = 1.83$ and $\bar{b} = 1.76$ with the error $S_0 t = 0.05$. So, combustion in the condensed phase of as K_3CrO_8 SHD has a high isoparametric pressure ($p \approx 60$ MPa). The physical component which appeared in the gas phase effect on SHD leads to the final value of $\hat{p}$, above which this component seems to be dominant. The extrapolated isoparametric point may not have a real sense, i.e., the process mechanism may change while approaching this point. Knowing the isoparametric pressure point and imposing restrictions upon the index ν of the ranges of the rate of the SHD of the substance due to additives may be estimated. Figure 3 shows the most probable ranges for the rate of K_3CrO_8 conversion due to the introduction of additives with restrictions $0 \leqslant \nu \leqslant 1$ imposed on ν.

For a quantitative description of the efficiency of the effect of various additives on K_3CrO_8 SHD, the index $\kappa = \log\frac{U_4}{U_{04}}$ was chosen (U_4 being the thermolysis wave propagation at 4.05 MPa in the sample with additive; U_{04} with the same value of p without additive) as it was found that at fixed pressure the rate of SHD depended linearly on the additive efficiency in accordance with eqn. (9). Here eqn. (8) holds (Fig. 4) in which a and $\hat{\kappa}$ are empirical coefficients specifying the coordinates of the isoparametric point

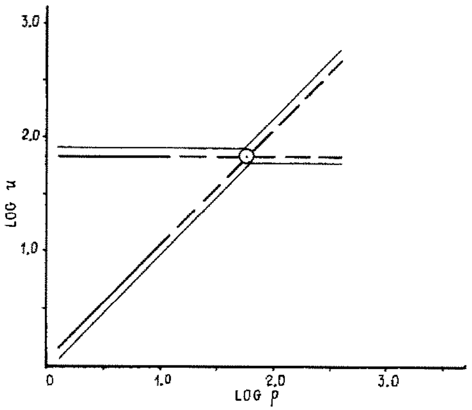

Fig. 3. Most probable ranges of K_3CrO_8 SHD rate taking into account the uncertainity of the isoparametric point. Broken lines are in the region of the extrapolation.

for the parameter κ. The parameter a in eqns. (3) and (8) proved to be approximately the same, thus supporting the applicability of the polynomial approximation in this case. Polynomial (10) has the following particular form

$$\log U = 1{,}83 - 0{,}37(1 - 0.57 \log p)(1 - 3.76\,\kappa) \qquad (11)$$

Note, that after reducing this polynomial to form (6), the numerical values of its coefficients differ somewhat from the coefficients of the polynomial obtained by direct application of the quantity b. This insignificant difference results from the fact that in the Exner method, the plot of log U vs. log p strictly form a pencil, thus violating the real position of the line for pure K_3CrO_8.

The above polynomial shows a satisfactory description (within ± 10% in the majority of cases) of the experimental data (Table 1) and may be used to estimate the K_3CrO_8 SHD dynamics in the pressure range studied by

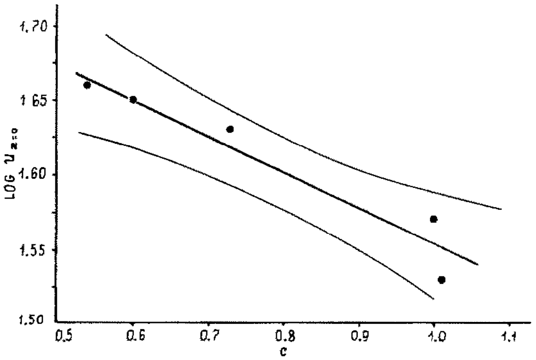

Fig. 4. Plot of the coefficients of eqn. (8) for K_3CrO_8-based mixtures.

introducing other additives with a measured κ. These additives may naturally leave the combustion mechanism essentially unchanged. In particular, for the mixture with PMMC the predicted value of U at 2.03 MPa differs from the measured value by more than 20%. As noted above, gas-phase reactions are important in this system.

The other additives (rosin and ferricenium reinekate) that accelerate K_3CrO_8 SHD may also decompose and evolve gaseous products. Rosin is more thermostable than PMMC, having as its main component abietic acid which is not very volatile and has a boiling point of, 523 K (1267 Pa). This promotes rosin oxidation in the condensed phase. Thermal decomposition of ferricenium reinekate was studied in ref. 13. This substance starts decomposing at 440 K. During thermolysis, this appreciable portion gives solid products (sulphocianides, sulphides), i.e., gas generation is comparatively low. The generated gas contains ammonia, which is difficult to oxidize. Solid products are oxidized easily. This is all responsible for the fact that in K_3CrO_8 mixtures the main reactions of ferricenium reinekate proceed with the participation of condensed substances, while gas-phase reactions are of secondary importance.

The PMMC data show that the error in assigning the K_3CrO_8 mixture with a new additive to a correlation series of type (11) for various substances results in a deviation of the predicted U value from the experimental value by 20–25%. If such an assumption is true then this deviation is less than 10%.

Comparison with the results from ref. 3 show that in calculations of U using the kinetic data of K_3CrO_8 thermolysis, then the error in E alone leads to a 100% difference in U at the confidence interval boundaries, this difference being even more appreciable if the error in the pre-exponent is taken into account. The use of b values results in an insignificant difference in this value at the confidence interval boundaries: at $p = 4.05$ and $\kappa = 0.25$, $\Delta U = 66.2 - 66 = 0.2$, i.e. $\approx 0.3\%$ and at $\kappa = -0.25$ the values of U actually coincide. Low sensitivity of polynomial (6) to the error in b with p^0 appropriately chosen to be $b - \log p^0 \gg 0$ can be derived from the terms in eqn. (6) including this value. Also note, that $\log \beta^0$ and ν^0 in eqn. (6) may be estimated with high accuracy by using a sufficient number of measurements. Thus, the main error in U calculations by the expressions of types (6) and (11) is attributed to the a priori prediction of the constant b with changing additive. However, because of low sensitivity to b, maximum error in this case is comparatively small (up to 25%). In the estimation of the cases when such errors appear, one may consider that such an additive may introduce principle changes in the combustion mechanism. A posteriori such changes are exposed in the violation of the correlations of the type (3).

The feasibility of isoparametric relations leading to polylinear functions has been shown earlier for some fuel mixtures [6]. The diversity of such examples proves the universal nature of the polylinear function in the quantitative description of self-propagating processes of the type discussed here.

REFERENCES

1 V.V. Sviridov, A.I. Lesnikovich, S.V. Levchik, K.K. Kovalenko and V.G. Guslev, Thermochim. Acta, 77 (1984) 341.
2 A.I. Lesnikovich, S.V. Levchik and V.G. Guslev, Thermochim. Acta, 77 (1984) 357.
3 A.I. Lesnikovich S.V. Levchik, K.K. Kovalenko and V.G. Guslev, Thermochim. Acta, 81 (1984) 245.
4 D.M. Himmelblau, Process Analysis by Statistical Methods, Wiley, New York, 1970.
5 V.A. Palm, Osnovy Kolichestvennoi Teorii Organicheskikh Reaktsii, Khimiya, Leningrad, 1977 (in Russian).
6 A.I. Lesnikovich, Fizika Goreniya i Vzryva, 15 (1979) 37 (in Russian).
7 A.I. Lesnikovich, Z. Fiz. Khim., 55 (1981) 1165 (in Russian).
8 A.I. Lesnikovich, K.K. Kovalenko, S.V. Levchik, Dokl. AN BSSR, 25 (1981) 438 (in Russian).
9 O. Exner, in A.S. Streitwieser, Jr. and R.W. Taft (Eds.), Progress in Physical and Organic Chemistry, Vol. 10, Wiley, New York, 1973, p. 411.
10 V.G. Guslev, K.K. Kovalenko, A.I. Lesnikovich and V.V. Sviridov, Fizika Goreniya i Vzryva, 12 (1976) 441 (in Russian).
11 A.A. Shidlovskii, Osnovy Pirotekhniki, Mashinostroyeniye, Moscow, 1964 (in Russian).
12 A.A. Polyakova and P.A. Khmelnitskii, Mass-Spektrometriya v Organicheskoi Khimii, Khimiya, Leningrad, 1972 (in Russian).
13 V.V. Sviridov, A.I. Lesnikovich, P.N. Gaponik, T.P. Adamovich, N.G. Litvinenko and V.G. Guslev, Z. Obsch. Khim., 46 (1976) 828 (in Russian).