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Note

# CORRELATION OF ACTIVATION ENERGIES OF LOW-TEMPERATURE THERMOLYSIS AND PHOTOLYSIS OF SOME FULMINATES WITH THEIR HEATS OF EXPLOSION

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The study of correlations of kinetic data of low-temperature thermolysis with detonation characteristics of individual organic explosives has been the subject of a number of papers [1–4]. Using the Polanyi–Semenov rule [5,6] as well as conclusions arrived at in the papers [2,3], a linear relationship was found for organic polynitro compounds [4]

$$E = C + aQ \qquad (1)$$

where $E$ is the activation energy (kJ $mol^{-1}$) of low-temperature thermolysis, $Q$ is the heat of explosion (kJ $g^{-1}$). Relationship (1) also holds for inorganic azides [7].

Using the activation energies of thermolysis and photolysis of sodium [8], silver [8], mercury [8,9] and thallous [8] fulminates, the validity of relationship (1) is verified in the present paper for both types of decomposition in the above-mentioned compounds. The necessary data are given in Table 1.

For the thermolysis of silver [8], mercury [9] and thallous [8] fulminates, the coefficients of relationship (1) were found: $C = 188.75$ kJ $mol^{-1}$; $a = -44.94$ g $mol^{-1}$; $r = 0.9944$; the standard error of estimate was 3.37; the average relative deviation was $\pm 1.51\%$. By means of this concrete form of relationship (1), the heat of explosion was calculated for sodium fulminate and the activation energy values for cadmium and copper(I) fulminates; these results are included in Table 1.

For the photolysis of sodium, mercury and thallous fulminates [8], the coefficients of relationship (1) were: $C = 13.68$ kJ $mol^{-1}$; $a = 3.86$ g $mol^{-1}$;

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TABLE 1

Survey of the data of the fulminates studied

| Fulminate | Heat of explosion | | Thermolysis | | | Photolysis | | |
|---|---|---|---|---|---|---|---|---|
| | $Q$ (kJ $g^{-1}$) | Ref. | Temperature range (K) | $E$ (kJ $mol^{-1}$) | Ref. | Temperature range (K) | $E$ (kJ $mol^{-1}$) | Ref. |
| $Na^+$ | 2.328 [a] | this work | 433–463 | 83.68 | 8 | 273–293 | 22.59 | 8 |
| $Cu^+$ | 2.125 | 10 | — | 93.25 [a] | this work | — | 21.90 [b] | this work |
| $Ag^+$ | 1.932 [c] | this work | 293–343 | 100.41 | 8 | 288–308 | 43.93 | 8 |
| | | | | | | — | 21.15 [b] | this work |
| $Cd^{2+}$ | 1.966 | 9 | — | 100.40 [a] | this work | — | 21.28 [b] | this work |
| $Hg^{2+}$ | 1.786 | 9 | — | 124.72 | 9 | 290–308 | 19.66 | 8 |
| | 1.493 | 12 | | | | | | |
| | 1.486 [d] | 13 | | | | | | |
| $Tl^+$ | 0.933 | 9 | 343–361 | 145.60 | 8 | 273–293 | 17.15 | 8 |

[a] Calculated by means of the form of eqn. (1) for thermolysis.
[b] Calculated by means of the form of eqn. (1) for photolysis.
[c] Calculated by means of the value $\Delta H_f = 179.07$ kJ $mol^{-1}$, taken from ref. 11.
[d] This $Q$ value best correlates in the sense of eqn. (1).

the standard error of estimate was 0.28; and the average relative deviation was ± 0.80%. The data of silver fulminate do not correlate with relationship (1); its photolysis was carried out under a different set of experimental conditions [8] to those of the three preceding fulminates. The activation energy values of silver, copper(I) and cadmium fulminates corresponding to the conditions of photolysis of sodium, mercury and thallous fulminates [8], were obtained by calculation using relationship (1) and are included in Table 1.

The rate of photolysis of the fulminates was followed as a function of intensity, i.e., as a function of the amount of absorbed radiation [8]. In the sense of the Polanyi–Semenov rule [5], this is in agreement with the positive gradient of relationship (1). On the other hand, exothermally thermolysing fulminates with gasometric detection of the reaction rate [8] are in agreement, in the sense of the same rule, with the negative gradient of relationship (1). The difference given above, however, does not exclude the identity of primary chemical processes of thermolysis and photolysis of the above-mentioned compounds.

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