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THERMAL DECOMPOSITION REACTION OF 3,3,6,6-TETRAMETHYL-1,2,4,5-TETROXANE IN 2-METHOXY-ETHANOL SOLUTION

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The thermal decomposition study of 3,3,6,6-tetramethyl-1,2,4,5-tetroxane (acetone cyclic diperoxide) was carried out in 2-methoxyethanol solution in the 130-166ºC temperature range. The overall reaction follows a first-order kinetic law up to at least 75% diperoxide conversion. The activation parameters ($\Delta H^{\#} = 22.5 \pm 0.7$ kcal·mol^{-1} *and* $\Delta S^{\#} = -25.6 \pm 0.5$ cal·mol^{-1}·K^{-1}) *for the unimolecular rupture of the O–O bond in the diperoxide molecule were obtained by measuring the remnant diperoxide at different reaction times by the CG technique. Acetone was detected by GC as the major organic product of the reaction.*

Keywords: acetone cyclic diperoxide, diacetone diperoxide, tetroxane, thermolysis.

Peroxides have wide commercial use as bleaching agents and polymerization catalysts [1]. Due to the weak O–O bond, peroxides undergo facile thermal decomposition to produce radicals. Many peroxides are shock sensitive and their overall decompositions are exothermic so that special handling precautions must be taken [2, 3]. Depending on the molecular stoichiometry of the peroxide, its decomposition may be explosive. Most peroxides, such as the commonly used dibenzoyl peroxide or di-*t*-butyl peroxide, contain too much carbon to be true explosives; but they have been rated as having a 2,4,6-trinitrotoluene (TNT) equivalence of 25 and 30%, respectively [4]. At the same time, the stoichiometry of hydrogen peroxide is perfect to allow it to act as an explosive; albeit, it does so only in concentrations exceeding those at which it is commonly available [5].

This study examines the decomposition behavior of multiperoxidic triacetone triperoxide (TATP) and compares it with that of 3,3,6,6-tetramethyl-1,2,4,5-tetroxane (acetone cyclic diperoxide, ACDP), both of which exhibit explosive behavior. In recent years, TATP has been used as an improvised explosive because its

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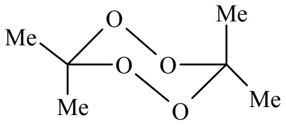
precursor chemicals are readily obtained and its synthesis is straightforward. The analysis and detection of one class of peroxide explosives have become particularly important in forensic investigations due to the emergence of terrorist threats and crimes in which these explosives were applied. Peroxide explosives are organic compounds that contain one or more peroxide functional groups (–O–O–), often in a cyclic form. In general, these compounds are powerful explosives, extremely sensitive to flame, heat, impact, and friction. Peroxide explosives can be generally prepared from hydrogen peroxide and a few other well-known chemicals such as ketones or aldehydes. A small amount of sulfuric or hydrochloric acid is added as a catalyst. Most of these ingredients can be obtained easily from local pharmacies.

The unusual reactivity of peroxides is generally attributed to weakness of the O–O bond, and it is expected that their thermal decomposition would be initiated by homolytic dissociation of the peroxide bond. Intuitively, it is expected that the peroxide-based explosives would liberate much energy upon decomposition, and their energy content depends on the carbon/oxygen ratio [6].

In this work a kinetic study of the thermal decomposition reaction of ACDP in 2-methoxyethanol (MOET) is presented.



ACDP

The thermal decomposition reaction of ACDP was studied in MOET solution at the temperature ranges of 130 to 166°C (Table 1, Fig. 1) and initial concentration *ca.* $2 \cdot 10^{-2}$ M. It was found that the kinetic behavior of this system is, according to the first-order kinetic law, up to at least *ca.* 75% of organic diperoxide conversions. It seems that under the experimental conditions of the present work, there are no contributions from the second-order processes inducing the ACDP decomposition at higher conversions.

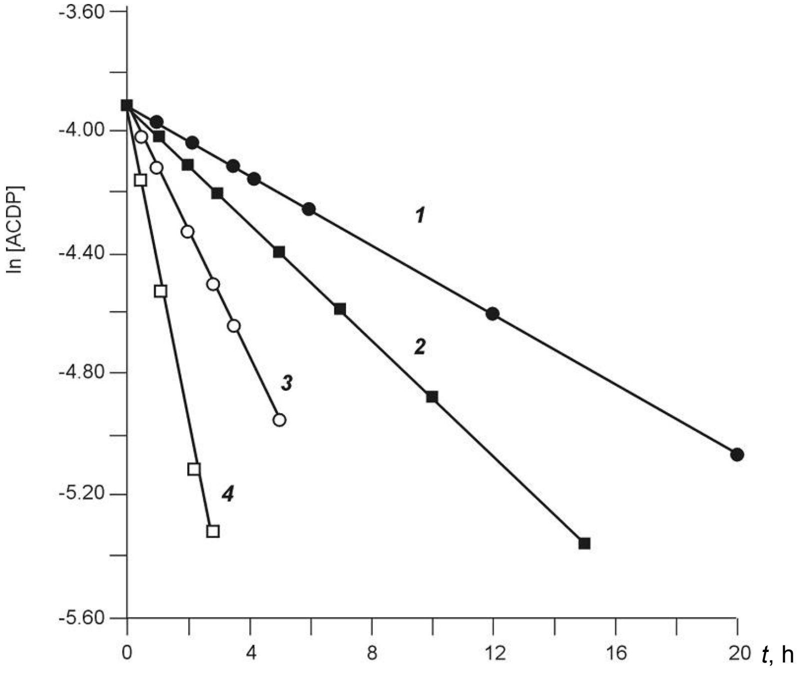


Fig. 1. Kinetics of ACDP thermal decomposition reaction ($2.0 \cdot 10^{-2}$ mol/l) in MOET solution at different temperatures: *1* – 130, *2* – 140, *3* – 150, *4* – 166°C.

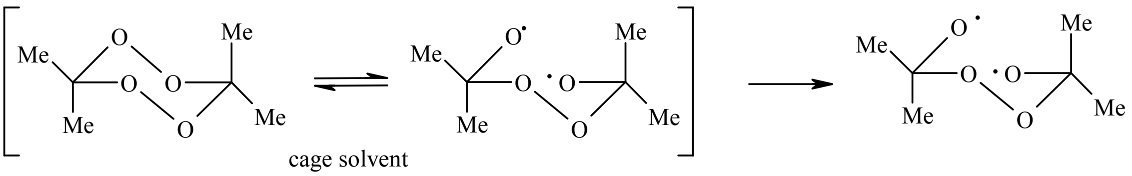
TABLE 1. Rate Constant Values for the Thermolysis of ACDP in MOET Solution

T, ºC	[ACDP]·10^2, mol/l	k_{exp}·10^5·s^{-1}
130	0.20	1.61
140	0.20	2.69
150	0.20	5.79
166	0.10	14.23
	0.20	14.17
	0.30	14.12

The temperature effect on the experimental rate constant values (k_{exp}) for the unimolecular reaction investigated can be represented by the following Arrhenius equations (Eq. (1)), where the errors shown are standard deviations from the least-mean-squares data treatment [11] and the activation energy is expressed in cal·mol^{-1}:

$$\ln k_{exp}\cdot s^{-1} = (17.9 \pm 0.5) - (23343 \pm 700)/RT \qquad (1)$$

The Arrhenius equation plot is linear (r = 0.997) in a relatively large temperature range (*ca.* 78°C), which suggests that the calculated activation parameter values for the ACDP reaction belong to a single process, which could be unimolecular thermal cleavage of the O–O bond.



The rate-determining step is the biradical formation, which further decomposes by either C–C, C–O, or O–O bond ruptures, leading to final organic products like acetone and molecular oxygen.

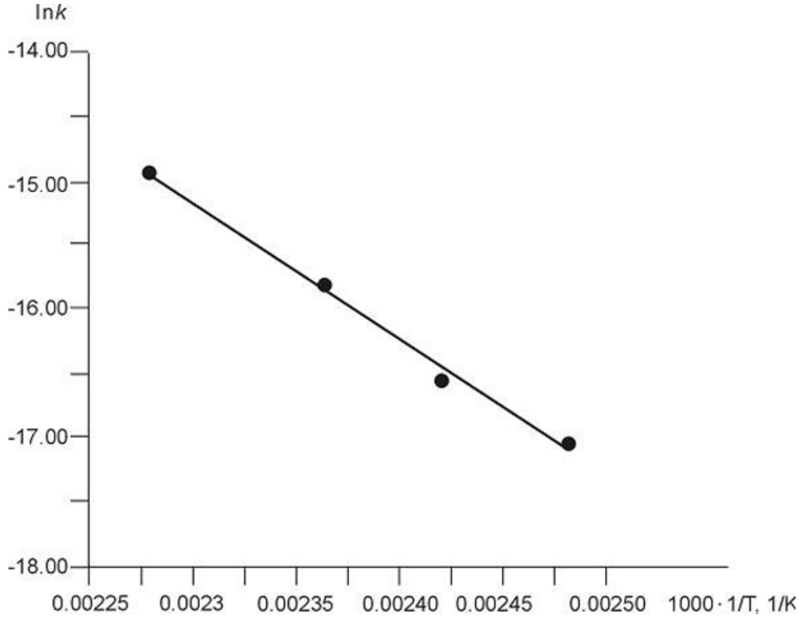
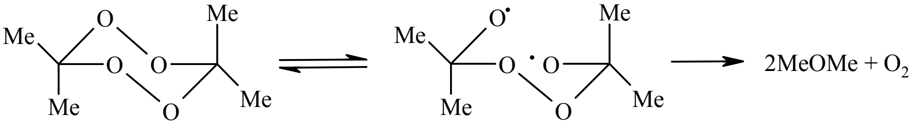


Fig. 2. Eyring plot corresponding to the thermal decomposition reaction of ACDP in MOET solution.

In the previous works it was demonstrated that the O–O bond dissociation energy is influenced by solvent [12], substituents [13], and ring size [14]. In the special case of these studies in different solvents, it was concluded that the activation parameters are higher in the more nonpolar solvents and the rate constant values are the lowest. The activation parameter values ($\Delta H^{\#}$ = 22.5 ± 0.7 kcal·mol^{-1} and $\Delta S^{\#}$ = -25.6 ± 0.5 cal·mol^{-1}·K^{-1}) (Fig. 2) corresponding to the unimolecular thermal decomposition reaction of ACDP in 2-methoxyethanol are in the order of those values obtained for other cyclic peroxides in polar solvents like methanol and 2-propanol [7, 14].

The thermolysis of ACDP in MOET solution follows the first-order kinetic law up to at least 75% diperoxide conversion. The activation parameters mentioned correspond to the initial homolysis of the O–O bond of the diperoxide molecule. Analysis of the reaction products is insufficient for proposing a complete mechanism of thermolysis of ACDP.



The high negative value of the change in entropy would explain the existence of a transition state. Such a result allows one to suppose the existence of an adduct, as was proposed for the kinetics of ACDP decomposition in 2-propanol [15].

EXPERIMENTAL

Analysis by gas chromatography was performed using a GC Hewlett-Packard instrument, series II plus (a capillary column HP5, 30 m×0.25 mm (i.d.), methylphenylsilicone stationary phase) with nitrogen as a carrier gas and flame ionization detection. The oven temperature was maintained at 40ºC for 3 min, then programmed at a rate of 30º/min to 150ºC.

IR absorption spectra at room temperature from 1 cm diameter pellets made of the compound diluted in spectroscopic grade KBr were recorded on an IR Nicolet infrared spectrometer using the diffuse reflectance technique between 400-4000 cm^{-1}.

3,3,6,6-Tetramethyl-1,2,4,5-tetroxane (ACDP) was prepared by dropwise addition of acetone (5 ml, 68.1 mmol) in acetonitrile (20 ml) to a vigorously stirred, cooled (-20°C) solution of 69.7% hydrogen peroxide (2.3 ml, 73.61 mmol) and sulfuric acid (5 ml, 18 M). After stirring at -20°C for 1 h, filtration, thorough water washing, and drying, the crude product (71% yield) was purified by recrystallization from ethyl acetate until a constant melting point of 133°C was attained. The product purity was also checked by GC and IR analyses (nujol), ν, cm^{-1}: 2910 (s), 2850 (s), 1200 (m), 940 (w), 860 (w), 814 (w), 682 (w) [7, 8].

The 2-Methoxyethanol used as solvent was purified with the appropriate techniques [9, 10] and its purity was checked by GC analysis.

Pyrex glass tubes (7 cm×6 mm o.d.) half filled with the appropriate ACDP solution were thoroughly degassed under vacuum at -196ºC and then sealed with a flame torch. To perform the runs the ampoules were immersed into the thermostatic silicone oil bath (±0.1ºC) and withdrawn after predetermined times, and the reaction was stopped by cooling them in an ice-water bath (0ºC). The ACDP remaining and the reaction products were determined by quantitative analysis by gas chromatography.

The qualitative determination of the organic reaction products was performed by GC. The corresponding first-order rate constant values were calculated from the slope of the line obtained by the mean-squares treatment of the reaction data when plotting the values of ln [ACDP] concentration *vs* reaction times. The activation parameters were calculated according to the Eyring equation, and the errors were worked out by the Arrhenius equation method using the mean-squares data treatment [11].

REFERENCES

1. J. Kroschwitz (editor), *Kirk-Othmer Concise Encyclopedia of Chemical Technology*, 4th ed., *Organic Peroxides*, Wiley, New York, Chichester, 1999, p. 1472.
2. S. M. Kaye (editor), *Encyclopedia of Explosives and Related Items*, PATR2700, Vol. 8, US Army Armament Research & Development Command, Dover, NJ, 1978, p. 203.
3. D. N. S. Hon, *Pulp Pap. Can.*, **86**, No. 6, 129 (1985).
4. T. Yoshida, K. Muraaga, T. Matsunaga, and M. Tamura, *J. Hazard. Mater.*, **12**, 27 (1985).
5. T. Urbanski, *Chemistry and Technology of Explosives*, Pergamon Press, Oxford, 1967, Vol. 3, p. 299.
6. F. Dubnikova, R. Kosloff, J. Almong, Y. Zeiri, R. Boese, H. Itzhaky, A. Alt, and E. Keinan, *J. Am. Chem. Soc.*, **127**, 1146 (2005).
7. L. A. C. Leiva, G. B. Castellanos, N. L. Jorge, L. F. R. Cafferata, and M. E. Gómez Vara, *Rev. Soc. Quím. Méx.*, **42**, 223 (1998).
8. A. H. Jubert, R. Pies Diez, and L. F. R. Cafferata, *J. Raman Spectr.*, **30**, 479 (1999).
9. J. A. Y. Riddick and W. B. Bunger, in: A. Weissberger (editor), *Organic Solvents*, Vol 2, Wiley Intersci., N.Y., 1970.
10. P.P. Perrin and W. L. F. Armarego, *Purification of Laboratory Chemicals*, Pergamon Press, 3rd ed., Oxford, 1988.
11. S. Huyberechts, A. Halleux, and P. Kruys, *Bull. Soc. Chim. Belg*., **64**, 203 (1955).
12. L. F. R. Cafferata, G. N. Eyler, E. L. Svartman, A. I. Cañizo, and E. E. Alvarez, *J. Org. Chem.* **56**, 411 (1991).
13. L. F. R. Cafferata, G. N. Eyler, E. L. Svartman, A. I. Cañizo, and E. J. Borkowski, *J. Org. Chem*., **55**, 1058 (1990).
14, A. I. Cañizo, N. E. Eyler, C. M. Mateo, E. E. Alvarez, and R. K. Nesprias, *Heterocycles*, **63**, 2231 (2004).
15. B. N. Moryganov, A. I. Kalinin, and L. N. Mikhotova, *J. Gen. Chem. (USSR)*, **32**, 3414 (1962).