*ISSN 1070-3632, Russian Journal of General Chemistry, 2009, Vol. 79, No. 10, pp. 2187–2190. © Pleiades Publishing, Ltd., 2009.*
*Published in Russian in Zhurnal Obshchei Khimii, 2009, Vol. 79, No. 10, pp. 1692–1696.*

# Thermal Decomposition of Formaldehyde Diperoxide in Aqueous Solution[1]

**S. A. I. Cazut[a], E. H. Ramírez Maisuls[a], M. R. Delfino[a], J. M. Romero[a],**
**N. L. Jorge[a], and E. A. Castro[b]**

[a] *Área Fisicoquímica, Facultad de Ciencias Exactas y Naturales y Agrimensura, UNNE, Campus Universitario,*
*Av. Libertad 5400, Corrientes, 3400 Argentina*
*phone/fax: +54(3783)457996; e-mail: lidianj@exa.unne.edu.ar*

[b] *INIFTA, División Química Teórica, Departamento de Química, Facultad de Ciencias Exactas,*
*Diagonal 113 y 64, Suc. 4, C.C. 16, La Plata, Buenos Aires, 1900 Argentina*
*phone: +54(2214)257430; fax: +54(2214)254642; e-mail: castro@quimica.unlp.edu.ar; eacast@gmail.com*

Received July 7, 2008

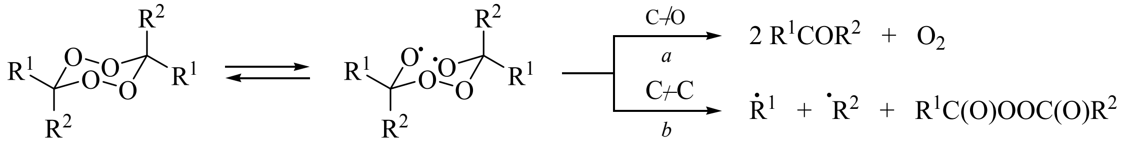
**Abstract**—Thermal decomposition of formaldehyde diperoxide (1,2,4,5-tetraoxane) in aqueous solution with an initial concentration of $6.22 \times 10^{-3}$ M was studied in the temperatures range from 403 to 439 K. The reaction was found to follow first-order kinetic law, and formaldehyde was the major decomposition product. The activation parameters of the initial step of the reaction ($\Delta H^{\neq} = 15.25 \pm 0.5$ kcal mol$^{-1}$, $\Delta S^{\neq} = -47.78 \pm 0.4$ cal mol$^{-1}$ K$^{-1}$, $E_a = 16.09 \pm 0.5$ kcal mol$^{-1}$) support a mechanism involving homolytic rupture of one peroxide bond in the 1,2,4,5-tetraoxane molecule with participation of the solvent and formation of a diradical intermediate.

**DOI:** 10.1134/S107036320910017X

Thermal decomposition of 1,2,4,5-tetroxane-substituted complexes has received considerable attention in recent years [1–5]. The chemistry of organic peroxides, which includes synthesis, characterization, and transformations of hydrogen peroxide derivatives, has a long history and rather strong traditions [6, 7]. Cyclic di- and tetraoxanes derived from aliphatic aldehydes and ketones, which were prepared in our laboratory, inspired numerous studies related to their application as explosives [8, 9]. In addition, studies on thermal decomposition of acetone diperoxide (ACDP) and formaldehyde diperoxide (FDP) have been initiated.

The reactivity of peroxides is generally attributed to lability of the O–O bond which readily undergoes homolytic dissociation constituting the rate-determining stage of the overall process (Scheme 1).

**Scheme 1.**



The reaction finally gives the corresponding ketone or aldehyde and oxygen via C–O bond cleavage in the primary diradical intermediate (path *a*). However, in some solvents C–C bond cleavage is observed (path *b*). When the reaction is carried out in hydrocarbons such as benzene or toluene, the major products are carbonyl compound and oxygen, while hydrocarbons are formed as minor ones [1, 2, 6, 7, 10–12]. These findings suggest recombination of intermediate radicals generated by homolytic cleavage of C–C bonds in the initial diradical. Thus, stepwise reaction mechanism has been postulated for thermolysis of tetraoxanes in different solvents, though a concerted process could not be ruled out (Scheme 2). This type of reaction has been

---

[1] The text was submitted by the authors in English.

**Table 1.** First– order constant values for DPF in aqueous solution

| Temperature, K | [FDP] × $10^3$, M | $k_{exp} \times 10^6$, $s^{-1}$ | $r^a$ |
|---|---|---|---|
| 403.0 | 6.22 | 1.62 | 0.9970 |
| 413.0 | 6.22 | 2.56 | 0.9970 |
| | 20.0 | 2.77 | 0.9970 |
| 423.0 | 6.22 | 4.27 | 0.9980 |
| 439.0 | 6.22 | $8.35^b$ | 0.9990 |

[a] Correlation coefficient from least mean square data treatment.
[b] Up to at least 80% DPF conversion.

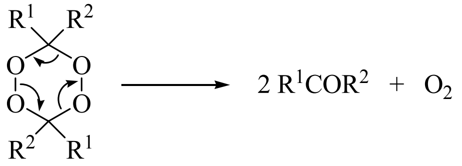
**Table 2.** Activation parameters for the thermolysis of DPF in aqueous solution[a]

| Solvent | $E_a$, kcal $mol^{-1}$ | $\Delta H^{\neq}$, kcal $mol^{-1}$ | $\Delta S^{\neq}$, cal $mol^{-1}$ $K^{-1}$ | $\Delta G^{\neq}$, kcal $mol^{-1}$ |
|---|---|---|---|---|
| Toluene | 22.80±0.9 | 21.90±0.9 | –16.30±1.2 | 28.71±0.9 |
| THF | 21.10±0.7 | 20.20±0.7 | –23.70±0.6 | 30.11±0.7 |
| Methanol | 14.80±0.8 | 14.00±0.8 | –39.40±0.8 | 32.02±0.8 |
| Water | 16.09±0.5 | 15.25±0.5 | –47.78±0.4 | 30.47±0.5 |

[a] The standard deviations were calculated as described in [13].

proposed for thermal decomposition of other cyclic peroxides [2, 10] but not for thermolysis of tetraoxanes.

**Scheme 2.**



In this work we examined the kinetics of thermal decomposition of 1,2,4,5-tetraoxane (formaldehyde diperoxide, FDP) in aqueous solution to assess the influence of solvent polarity on the initial reaction stage. The data were compared with those obtained in previous studies.

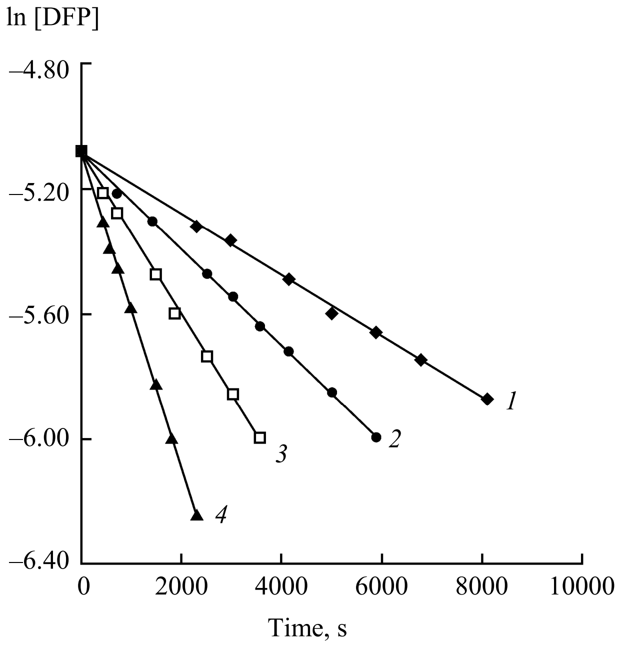


**Fig. 1.** Semilog kinetic plots for the decomposition of formaldehyde diperoxide ($c_0$ = $6.22 \times 10^{-3}$ M) in aqueous solution at (*1*) 403, (*2*) 413, (*3*) 423, and (*4*) 439 K.

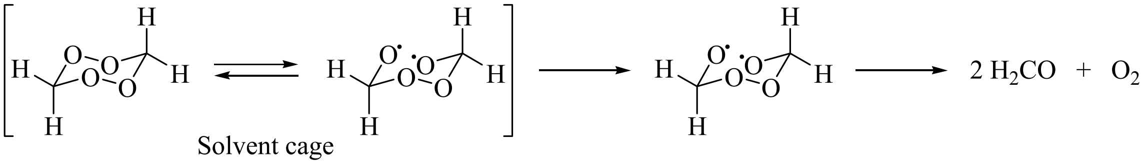
The thermolysis of FDP in aqueous solution at an initial concentration of $6.2 \times 10^{-3}$ M in the temperature range grom 403 to 439 K follows first-order kinetic law until ~60% conversion (Table 1, Fig. 1). The activation parameters for the thermolysis of FDP in aqueous solution were similar to those obtained in other solvents (Table 2). To exclude contribution of a radical-induced decomposition as a competing mechanism, the kinetics of thermal decomposition of FDP in water were studied at 140°C at a higher initial substrate concentration (0.2 M, Table 1). The results showed that the rate constants are independent of the initial concentration. The reaction carried out at 166°C (initial FDP concentration $6.2 \times 10^{-3}$ M) followed first-order kinetics up to at least 80% conversion (Fig. 1). These data suggest that there is no contribution from any secondary process to decomposition of FDP at higher conversion.

The nature of the products (formaldehyde) indicates the lack of other decomposition processes and supports the assertion that the rate constants actually correspond to unimolecular homolysis. However, radical-initiated decomposition process cannot be ruled out at higher temperatures and higher initial substrate concentrations. The temperature effect on the *k* values can be represented by Eq. (1).

$$\ln k\,(s^{-1}) = (6.76 \pm 0.4) - (8098.24 \pm 0.5)\,T^{-1}. \quad (1)$$

The corresponding plot is linear ($r$ = 0.999) over a relatively wide temperature range ($\Delta T$ = 36 K); therefore, the calculated activation parameters for FDP decomposition in aqueous solution belong to a single process which could be unimolecular homolysis. The results of AM1 semiempirical calculations with full geometry optimization [11, 12] also supported the stepwise mechanism of formaldehyde diperoxide decomposition through intermediate diradical species. The calculated energy barrier for the concerted uni-

**Scheme 3.**



molecular decomposition turn out to be higher by ~20 kcal $mol^{-1}$ higher than the barrier to unimolecular homolytic O–O bond cleavage (stepwise diradical-initiated decomposition, ~21 kcal $mol^{-1}$).

Thus, the thermolysis of diperoxides in aqueous solution can be represented by Scheme 3, where the rate of tetraoxane ring opening inside a solvent cage is relatively fast. The subsequent cleavage of C–O bonds in the intermediate diradical yields two formaldehyde and oxygen molecules.

A considerable solvent effect on the thermal decomposition of FDP should be noted. Polar solvents could facilitate peroxide bond rupture, thus lowering the activation parameters by ~20 kcal $mol^{-1}$. Weakly polar solvents should not affect the transition state, so that the activation energy may be expected to be similar to that obtained in the gas phase [14]. In fact, the thermal decomposition of FDP in toluene and tetrahydrofuran showed analogous activation parameters (Table 2). The Gibbs energies of activation ($\Delta G^{\neq}$) found for the thermal decomposition of FDP in water and other solvents turned out to be nearly similar (Fig. 2, Table 2), indicating qualitatively analogous interactions between the solute and solvent molecules in the initial thermolysis step. The enthalpy of activation decreases in going from weakly polar solvents to strongly polar ones. On the other hand, the entropy of activation increases in absolute value, so that the enthalpy–entropy compensation effect is observed. The activation parameters are in agreement with the stepwise mechanism involving homolytic cleavage of one peroxide bond in FDP with formation of diradical intermediate, as was observed for other analogous reactions [15–17].

Quantitative analysis of the thermolysis products showed formation of 2 mol of formaldehyde per mole of FDP, regardless of the temperature. Insofar as concerted mechanism of decomposition may be ruled out, the formation of the thermolysis products can be interpreted in terms of initial homolytic cleavage of the O–O bond to give diradical **A** (Scheme 3) which can rebuild FDP molecule or undergo subsequent cleavage of the C–O bond with formation of formaldehyde and oxygen molecules. Presumably, generation of the diradical occurs in a solvent cage, and solvent molecules facilitate the subsequent C–O bond cleavage.

Thus the thermal decomposition of formaldehyde diperoxide in water solution follows first-order kinetic law up to at least 60% substrate conversion. The activation parameters correspond to unimolecular process. The mechanism of FDP thermolysis in aqueous solution conforms to that proposed previously for tetraoxanes and includes initial homolytic dissociation of the peroxide bond with formation of intermediate diradical and subsequent C–O bond cleavage to produce two formaldehyde molecules and one oxygen molecule as final products. Solvents exert a significant effect on the entropy of activation of the examined reaction. The large and negative entropies of activation ($\Delta S^{\neq}$ = –49.8 cal $mol^{-1}$ $K^{-1}$ in water) suggests formation of an adduct by solvent molecules and FDP.

## EXPERIMENTAL

Formaldehyde diperoxide was prepared by standard methods [11, 12], and its purity was checked by GLC.

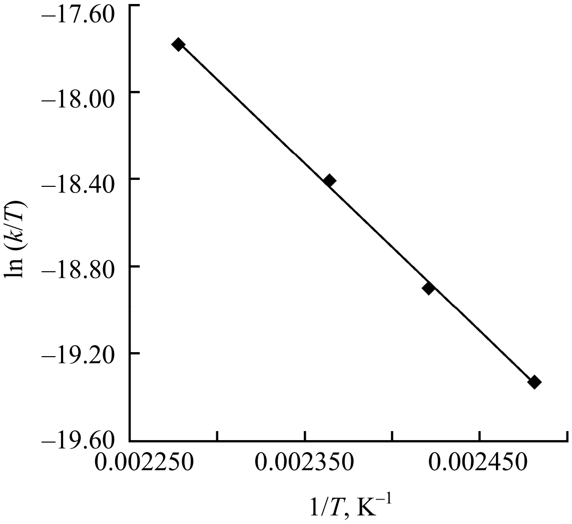


**Fig. 2.** Eyring plot for thermal decomposition of formaldehyde diperoxide in aqueous solution.

*n*-Octane of analytical grade (Fluka) was used as internal standard in quantitative determination of FDP and other products.

Pyrex glass ampules (12 cm long and 4 mm i.d.) were filled with 0.2 ml of FDP solutions, thoroughly degassed under reduced pressure at 77 K, and sealed using a flame torch. The ampules were immersed into a silicone oil bath maintain at a required temperature with an accuracy of ± 0.1K and withdrawn after 5–10 min at each temperature, and the reaction was stopped by cooling to 273 K. The unreacted FDP and reaction products were determined by GLC analysis on Hewlett–Packard 5890 Series II gas chromatograph (flame ionization detector; HP-5 capillary column, 30 m × 0.25 mm, stationary phase 5% phenylmethylsilicone, carrier gas nitrogen; injector temperature 378 K, oven temperature programming from 313 to 423 K at a rate of 30 deg $\text{min}^{-1}$). The products were identified by comparing their retention times with those of authentic samples or by comparing the corresponding mass spectra (in this case helium was used as carrier gas, and a Hewlett–Packard 5972A mass-selective detector was connected to the chromatograph).

The first-order rate constants were calculated from the slope of the plots of ln [DPF] values versus reaction time. In all cases, the reaction progress was monitored for at least one half-conversion period. The corresponding energies of activation were determined from the Arrhenius equation, followed by the least-squares processing [13, 18]. The other activation parameters ($\Delta H^{\neq}$, $\Delta S^{\neq}$, $\Delta G^{\neq}$) were calculated by the Eyring equation.

## REFERENCES

1. Cafferata, L.F.R. and Furlong, J.J., *Advances in Oxygenated Processes*, Baumstark, A.L., Ed., Greenwich, CT: JAI, 1995, vol. 4, p. 81.
2. Cafferata, L.F.R., Eyler, G.N., and Mirífico, M.V., *J. Org. Chem.*, 1984, vol. 49, p. 2107.
3. Jorge, N.L., *Doctoral Thesis*, 1997, UNLP, Argentina.
4. Jorge, N.L., Gómez Vara, M.E., Castro, E.A., Autino, J.C., and Cafferata, L.F.R., *J. Mol. Struct. (Theochem)*, 1999, vol. 459, p. 29.
5. Jorge, N.L., Peruchena, N.M., Castro, E.A., and Cafferata, L.F.R., *J. Mol. Struct. (Theochem)*, 1998, vol. 433, p. 311.
6. McCullough, K.J., Morgan, A.R., Nonhebel, D.C., and Pauson, P.L., *J. Chem. Res., Synop.*, 1980, no. 2, p. 36.
7. McCullough, K.J., Morgan, A.R., Nonhebel, D.C., Pauson, P.L., and White, C.J., *J. Chem. Res., Synop.*, 1980, no. 2, p. 34.
8. Dubnikova, F., Kosloff, R., Almog, J., Zeiri, Y., Boese, R., Itzhaky, H., and Keinan, E., *J. Am. Chem. Soc.*, 2005, vol. 127, p. 1146.
9. Van Duin, A.C., Zeiri, Y., Dubnikova, F., Kosloff, R., and Goddard, W.A., *J. Am. Chem. Soc.*, 2005, vol. 127, p. 11053.
10. Cañizo, A.I. and Cafferata, L.F.R., *Anal. Asoc. Quim. Argentina*, 1992, vol. 80, no. 4, p. 345.
11. Jorge, N.L., Leiva, L.C.A., Romero, J.M., and Gómez Vara, M.E., *Rev. Int. Inform. Tecnol.*, 2002, vol. 13, no. 2, p. 23.
12. Jorge, N.L., Leiva, L.C.A., Romero, J.M., Gómez-Vara, M.E., Hernández-Laguna, A., and Cafferata, L.F.R., *http://www1.unne.edu.ar/cyt/2002/cyt.htm.e037*.
13. Huyberechts, S., Halleux, A., and Kruys, P., *Bull. Soc. Chim. Belg.*, 1955, vol. 64, p. 203.
14. Cafferata, L.F.R. and Lombardo, J.D., *Int. J. Chem. Kinet.*, 1994, vol. 26, p. 503.
15. Cafferata, L.F.R., Eyler, G.N., Svartman, E.L., Cañizo, A.I., and Alvarez, E.E., *J. Org. Chem.*, 1991, vol. 56, p. 411.
16. Leiva, L.C., Castellanos, M.G., Jorge, N.L., Cafferata, L.F.R., and Gómez Vara, M.E., *Rev. Soc. Quim. México*, 1998, vol. 42, p. 223.
17. Leiva, L.C., Cafferata, L.F.R., and Gómez Vara, M.E., *Anal. Asoc. Quim. Argentina*, 2000, vol. 88, no. 1/2, p. 9.
18. Schaleger, L.L. and Long, F.A., *Adv. Phys. Org. Chem.*,