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Rates of Thermal Decomposition of *t*-Butyl Peroxypivalate

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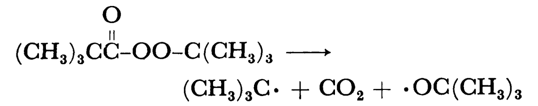
Synopsis. The kinetics of decomposition of *t*-butyl peroxypivalate in benzene, hexane and mineral spirits were determined iodometrically in the temperature range 50—75°. The decomposition in benzene indicated smaller rate constants and activation parameters than those in hexane or mineral spirits. The solvated transition state in aromatic solvent is discussed on the basis of these results and the previously published data.

The rate constants of decomposition of *t*-butyl peroxypivalate which decomposes with a concerted mechanism have been used as standard of those of other peroxyesters.1)



$$(CH_3)_3C\overset{O}{\overset{\|}{C}}\text{-OO-}C(CH_3)_3 \longrightarrow (CH_3)_3C\cdot + CO_2 + \cdot OC(CH_3)_3 \qquad (1)$$

However, different values of the activation parameter in the decomposition have been reported by several investigators.2) For instance, Lorand and coworkers2a) obtained $\Delta H^{\neq}=115\,\mathrm{kJ\,mol^{-1}}$ and $\Delta S^{\neq}=15\,\mathrm{JK^{-1}\,mol^{-1}}$ in cumene, but Fort and Franklin2b) reported $\Delta H^{\neq}=107\,\mathrm{kJ\,mol^{-1}}$ and $\Delta S^{\neq}=-11\,\mathrm{JK^{-1}\,mol^{-1}}$ in the same solvent. These conflicting values give rise to some difficulty on studying the decomposition mechanism of peroxyesters.

We measured the rates of the decomposition of *t*-butyl peroxypivalate in benzene, hexane and mineral spirits, and also reevaluated the previously published data.

Table 1. Rates of decomposition of *t*-butyl peroxypivalate

Initial concentration M†	Temperature °C	Rate constant k×10⁵/s⁻¹
	Solvent: Benzene	
0.10	50	1.03
0.10	55	1.94
0.10	60	3.92
0.21	60	3.89
0.10	65	7.31
0.20	65	7.19
0.10	70	13.0
	Solvent: Hexane	
0.10	55	0.842
0.10	60	1.59
0.10	65	3.39
0.10	70	6.19
	Solvent: Mineral spirits	
0.10	55	1.01
0.10	60	2.15
0.10	65	4.14
0.10	70	7.58
0.10	75	14.7

† 1M=1 mol dm⁻³.

Results and Discussion

The rates of the decomposition of *t*-butyl peroxypivalate were determined by following the disappearance of the peroxide with iodometric titration. The results yielded good first order kinetics and were independent of initial peroxide concentration. These ruled

Table 2. Activation parameters for the decomposition of *t*-butyl peroxypivalate

Solvent	$\Delta H^{\neq}$ kJmol⁻¹	$\Delta S^{\neq}$ JK⁻¹mol⁻¹	k×10⁵at 60°C/s⁻¹	Rel. rate at 60°C
Hexane	125±3	40± 8	1.59	1.0
Mineral spirits	123±4	33±11	2.15	1.4
Cyclohexane[a]	123±6	33±17	2.06	1.3
Cumene[b]	118±1	23±10	2.95	1.6
Benzene	115±1	14± 3	3.82	2.1

a) See Ref. 2a. b) Reevaluated from published data (See Fig. 1.).

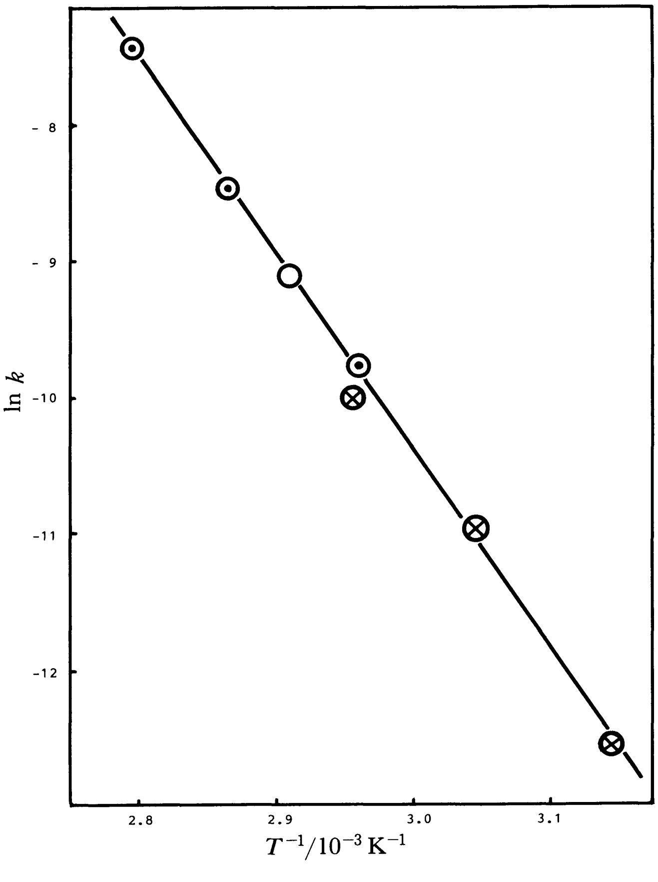


Fig. 1. Arrhenius plot of published data on thermal decomposition of *t*-butyl peroxypivalate in cumene: (⊙) data points of Lorand *et al.*2a) (○) data points of Fort *et al.*2b) (○) data point of Ernst *et al.*2c)

out radical induced decomposition under our experimental conditions. Table 1 shows the obtained data. The activation parameters were calculated from the data of the table and given in Table 2.

We also reevaluate the decomposition rates in cumene using the early published data. The data were plotted in Fig. 1 and the activation parameters were recalculated to be also shown in Table 2. A remarkable good Arrhenius plot in the figure shows that the differences between the activation parameters in each report are due to small systematic errors occurring within each set of experiments.

The rates of homolytic decomposition of *t*-butyl peroxypivalate were affected by solvents. It decomposes about twice faster in polarizable solvents such as benzene and cumene than aliphatic hydrocarbons having low polarizability. This could be explained by strong interactions of the aromatic solvent with *t*-butyl peroxypivalate at the transition state.[3] The observed decreases of the $\Delta H^{\neq}$ and $\Delta S^{\neq}$ in the aromatic solvents relative to those in the aliphatic hydrocarbons support this solvated transition state. Similar results have been reported in the thermal decomposition of diacyl peroxides,[4] di-*t*-butyl peroxide and *t*-butyl α-(*p*-substituted phenyl) peroxyisobutyrate.[6]

Experimental

t-Butyl peroxypivalate, benzene, hexane and mineral spirits were commercial materials. The rates of decomposition were measured by monitoring the undecomposed peroxyester with iodometric titration. A weighed amount of the peroxyester solution was added to glacial acetic acid solution containing saturated aqueous sodium iodide solution and a small amount of iron(III) chloride, and allowed to stand at room temperature for 15 min. Then the iodide liberated was titrated with aqueous sodium thiosulfate solution.

References

1) P. D. Bartlett and D. M. Simons, *J. Am. Chem. Soc.*, **82**, 1753 (1960).

2) a) J. P. Lorand, S. D. Chadroff, and R. W. Wallace, *J. Am. Chem. Soc.*, **90**, 5266 (1968); b) R. C. Fort, Jr. and R. E. Franklin, *J. Am. Chem. Soc.*, **90**, 5267 (1968); c) J. A. Ernst, C. Thankachan, and T. T. Tidwell, *J. Org. Chem.*, **39**, 3614 (1974); d) D. D. Tanner, H. Yabuuchi, and H. Lutzer, *Can. J. Chem.*, **55**, 617 (1977).

3) One possibility which is considered as the interactions is an electron transfer from the solvent to the peroxide such as:

$$[(CH_3)_3C\cdot CO_2:OC(CH_3)_3]^{-}[\quad]^{+}$$

4) a) R. C. Lamb, L. L. Vestal, G. R. Cipau, and S. Debnath, *J. Org. Chem.*, **39**, 2096 (1974); b) J. Koo and G. B. Schuster, *J. Am. Chem. Soc.*, **99**, 6107 (1977).

5) E. S. Huyser and R. M. VanScoy, *J. Org. Chem.*, **33**, 3524 (1968).

6) J. P. Engstrom and J. C. DuBose, *J. Org. Chem.*, **38**, 3817 (1973).