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ACTIVATION PARAMETERS FOR THE DECOMPOSITION OF 3,3-DIMETHYL-1,2-DIOXETANE IN 60% AQUEOUS METHANOL

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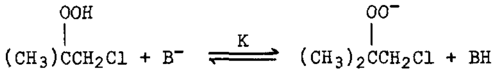
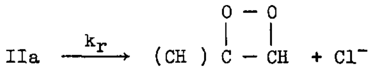
We had originally proposed that a 1,2-dioxetane intermediate was generated in the basic decomposition of a β-halohydroperoxide (1). Other reactions of this type have been reported since then, some of which may be interpreted as passing through 1,2-dioxetane intermediates (2). The use of this type of reaction by Kopecky and Mumford (3) has led to the isolation of 3,3,4-trimethyl-1,2-dioxetane (I). In carbon tetrachloride, the activation parameters for thermal decomposition of I are $E_a = 23.7$ kcal/mole and log $A = 12.2$ (4). Our gas phase thermochemical calculations substantiate the reported activation parameters (5). We now report the results of a kinetic analysis of the basic decomposition of chloro-<u>t</u>-butyl hydroperoxide (II) in 60% aqueous methanol, which yields the activation parameters for decomposition of 3,3-dimethyl-1,2-dioxetane (III) in this solvent.

A mechanism which is consistent with the kinetic analysis, product study and light emission in the basic decomposition of II is shown below. With chloride as the leaving group, ring closure (eq 2) is slow compared to gragmentation of the 1,2-dioxetane (eq 3). Thus, iodometric kinetic data provide information about K and k_r (eq 1 and 2). Light emission will supply information about k_f, since eq 4 will be fast compared to eq 3. The observed rate coefficient obtained from iodometric data (k_{obs}) and k_f are treated as rate coefficients from two series



$$(CH_3)\overset{OOH}{C}CH_2Cl + B^- \underset{}{\overset{K}{\rightleftharpoons}} (CH_3)_2\overset{OO^-}{C}CH_2Cl + BH \qquad (1)$$

II IIa



$$IIa \xrightarrow{k_r} (CH\ \ )\ C - CH + Cl^- \qquad (2)$$

III

$$III \xrightarrow{k_f} [(CH_3)_2CO \cdot CH_2O]^* \qquad (3)$$

IV

$$IV \longrightarrow (CH_3)_2CO + CH_2O + h\nu \qquad (4)$$

first-order reactions. The time (t_{max}) at which maximum light emission occurs is used in conjunction with k_{obs} to calculate k_f (6). A Beckman DU, equipped with an RCA 1P28 phototube and output to a recorder, was used to measure total light emission. The emission spectrum of a similar system was reported previously (3). In some instances, 8.00 × 10^{-3} M fluorescein was added to increase the light intensity; however t_{max} values were unchanged with added fluorescein. To demonstrate that the iodometric rate coefficient (k_{obs}), which is a measure of total peroxide concentration, was unaffected by the low concentrations of the intermediate 1,2-dioxetane, k_{obs} was also determined by the rate of chloro-t-butyl hydroperoxide disappearance. The specific analysis for the hydroperoxide was made by gas-liquid chromatography (glc), whereby reproducible amounts of the corresponding isobutylene chlorohydrin were measured by comparison to an internal standard. At 30.00° with the conditions given in Table I, the glc method gave $k_{obs} = 2.10 \pm .07 \times 10^{-3}\ sec^{-1}$, which is in excellent agreement with the fourth entry in Table I. As a check on the method, concentration vs time profiles of III were generated by a numerical integration program utilizing an IBM 1130 computer and a Calcomp plotter. The input parameters were initial concentrations, K, k_r and k_f. The values of K and k_f were obtained from a kinetic analysis of the effect of base concentration on the reaction. The t_{max} values, obtained from emission studies and those from the calculated concentration vs time profile of III, are in good agreement (Table I).

Table I. Kinetic Data Derived from the Basic Decomposition of Chloro-*t*-butyl Hydroperoxide in Aqueous Methanol[a]

Temp, °C	10^3k_{obs},sec^{-1}	10^3k_f,sec^{-1}	t_{max},sec	
			Obsd	Calcd
15.68	0.295	2.26	1038	996
20.32	0.575	3.66	600	596
25.23	1.15	5.35	366	362
30.03	2.19	9.00	208	202
34.90	4.17	14.1	122	116
39.80	7.94	21.9	72.9	72

[a] [II] = 0.0100 *M*, $[B^-]$ = 1.58 *M*, μ = 1.58 *M*, corrected temperatures.

From the tabulated values of k_f, the activation parameters for decomposition of III in 60% aqueous methanol are calculated to be: E_a = 16.9 ± 0.2 kcal/mole (r = 0.999), log A = 10.13, $\Delta H^{\ddagger}$ = 16.3 ± 0.2 kcal/mole and $\Delta S^{\ddagger}$ = -14.2 ± 0.8 eu. The activation parameters for III in aqueous methanol solvent are significantly lower than those calculated for the gas phase (5): E_a = 22.9 kcal/mole and log A = 12.9. Such a solvent effect is reasonable, by analogy to the fragmentation of *t*-butoxy radicals. Here, an uncharged *t*-butoxy radical decomposes to give one carbonyl molecule (acetone) and a methyl radical. The activation energy is lowered by 8 kcal/mole in changing from an aprotic (carbon tetrachloride) to a protic solvent (acetic acid)(7). In the decomposition of III, an uncharged molecule yields two carbonyl molecules and the activation energy is lowered by 6 kcal/mole in proceeding from the gas phase to a polar protic solvent. The low log A value in aqueous methanol as compared to the gas phase is also consistent with solvation effects.

The technique for determining the rate of decomposition of III *in situ* is currently being applied to other systems and the details will be reported in the future.

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