Decomposition Kinetics of Isopropyl *tert*-Butyl Peroxide[1]

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In general, thermal decompositions of di-*tert*-alkyl peroxides occur by the unimolecular homolytic cleavage of the oxygen–oxygen linkage of the peroxide functionality.[2] Similarly, radical induced decompositions of di-*tert*-alkyl peroxides generally involve attack by the radical at the peroxide functionality.[3] In contrast, the chemistry of primary and secondary alkyl peroxides suggests extensive involvement of the α hydrogens of the alkyl groups in their decompositions as evidenced by the formation of molecular hydrogen in intramolecular, nonradical forming, decomposition reactions.[4] Hydrogen formation via an intramolecular decomposition is not possible for dialkyl peroxides having one tertiary alkyl group and, therefore, only one primary or secondary alkyl group. Hiatt and his co-workers[5] found, for example, that *tert*-butyl diphenylmethyl peroxide yielded no molecular hydrogen on decomposition. They also reported that the thermolysis was a first-order reaction with kinetic parameters that suggested that decomposition proceeded by unimolecular cleavage of the oxygen–oxygen linkage of the peroxide functionality. These observations suggest that the decomposition of *tert*-butyl diphenylmethyl peroxide, at least, does not involve reaction of the α hydrogen of the diphenylmethyl moiety in the rate-determining process.

Our investigation of the thermal decompositions of isopropyl *tert*-butyl perioxide (**1**) indicate that induced decompositions of this peroxide do occur. Both the kinetics of the decompositions in different solvents as well as the distributions of the reaction products suggest that the induced decomposition involves attack of an α hydrogen on the isopropyl moiety of **1** by a peroxide-derived *tert*-butoxyl radical.

Results and Discussion

Decomposition of isopropyl *tert*-butyl peroxide in both *tert*-butylbenzene and cumene at 135 °C yielded isopropyl alcohol, acetone, and *tert*-butyl alcohol as the major reaction products (eq 1–4) (see Table I). The observed reaction products could be explained in terms of the reactions with the solvent of the isopropoxyl and *tert*-butoxyl radicals formed by the unimolecular thermolysis of **1**. The sum of the amounts of acetone, isopropyl alcohol, and *tert*-butyl alcohol is, in both solvents, equal to twice the amount of peroxide that has decomposed. However, the more rapid rate of decomposition of the peroxide in *tert*-butylbenzene relative to its decomposition rate in cumene and the higher acetone/isopropyl alcohol ratio found in the decompositions in *tert*-butylbenzene indicate that decomposition mechanism(s) other than the unimolecular homolysis shown in eq 1 likely are operative.

$$\underset{\mathbf{1}}{(CH_3)_3COOCH(CH_3)_2} \longrightarrow (CH_3)_3CO\cdot + \cdot OCH(CH_3)_2 \qquad (1)$$

$$(CH_3)_3CO\cdot \longrightarrow (CH_3)_2C{=}O + CH_3\cdot \xrightarrow{RH} CH_4 + R\cdot \qquad (2)$$

$$(CH_3)_3CO\cdot + RH \rightarrow (CH_3)_3COH + R\cdot \qquad (3)$$

$$(CH_3)_2CHO\cdot + RH \rightarrow (CH_3)_2CHOH + R\cdot \qquad (4)$$

The good agreement between the amounts of decomposition products formed and the peroxide that has decomposed, as well as the absence of any detectable amounts of acetaldehyde among the reaction products, indicate that the isopropoxyl radical does not fragment (eq 5) to any significant extent, but likely participates only in hydrogen abstraction reactions to yield isopropyl alcohol. The amount of isopropyl alcohol formed, therefore, serves as a measure of the extent of unimolecular decomposition of the peroxide (27% in *tert*-butylbenzene and 59% in cumene at 135 °C). Consequently, about 73% of the peroxide decomposes in *tert*-butylbenzene by some route that does not involve formation of the isopropoxyl radical, whereas only about 40% of the peroxide follows a similar path of decomposition in cumene.

Table I. Decompositions of 1 in Cumene and *tert*-Butylbenzene

Time, min	Peroxide remaining, mmol	Products, mmol		
		Acetone	Isopropyl alcohol	*tert*-Butyl alcohol
		Cumene[a]		
0	1.22			
40	1.11	0.07	0.05	0.11
80	1.00	0.13	0.12	0.19
120	0.91	0.18	0.17	0.26
160	0.82	0.22	0.23	0.33
200	0.75	0.28	0.28	0.41
243	0.67	0.33	0.34	0.46
280	0.62	0.35	0.37	0.49
320	0.56	0.41	0.39	0.56
		tert-Butylbenzene[a]		
0	1.11			
40	0.92	0.26	0.03	0.10
80	0.78	0.45	0.08	0.22
120	0.65	0.57	0.09	0.27
160	0.55	0.67	0.13	0.33
200	0.49	0.74	0.14	0.37
243	0.42	0.82	0.18	0.39
280	0.37	0.88	0.18	0.42
320	0.34	0.89	0.21	0.46

[a] Solvent/peroxide = 5:1.

$$(CH_3)_2CHO\cdot \rightarrow CH_3CHO + CH_3\cdot \qquad (5)$$

The induced decomposition of the peroxide via the chain sequence shown in eq 6 and 7 accounts for the formation of acetone from the isopropoxyl moiety of the peroxide. The extent of the induced decomposition is dependent on the partitioning of the hydrogen abstraction reactions of the *tert*-butoxyl radical between the peroxide and the solvent. The extent of induced decomposition would be expected, as observed, to be less in cumene, which has a benzylic hydrogen atom that is comparatively more reactive toward reaction with the *tert*-butoxyl radical, than in *tert*-butylbenzene which has only the less reactive primary alkyl hydrogens.

$$(CH_3)_3CO\cdot \text{ (or } CH_3\cdot) + (CH_3)_2CHOOC(CH_3)_3 \xrightarrow{k_6} (CH_3)_3COH \text{ (or } CH_4) + \underset{\mathbf{2}}{(CH_3)_2\dot{C}OOC(CH_3)_3} \qquad (6)$$

$$(CH_3)_2\dot{C}OOC(CH_3)_3 \xrightarrow{k_7} (CH_3)_2C{=}O + (CH_3)_3CO\cdot \qquad (7)$$

$$((CH_3)_3CO\cdot \rightarrow (CH_3)_2C{=}O + CH_3\cdot) \qquad (8)$$

The rate laws for the decompositions of **1** in these solvents are the combined rates for the unimolecular decomposition and the induced decomposition.

$$-d[Per]/dt = k_1[Per] + k_6[(CH_3)_3CO\cdot][Per] \qquad (9)$$

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The observed kinetic order of the peroxide in these decomposition reactions would depend both on the extent of the contribution of the induced decomposition to the overall rate *and* on the rate-limiting step (or steps) in the chain sequence (eq 6 and 7) for the induced decomposition. Thus, if the unimolecular fragmentation of the radical **2** in reaction 7 is the rate-limiting step of the chain sequence, the steady-state concentration of **2** would be greater than that of the *tert*-butoxyl radical and termination of the chain would be a bimolecular interaction of **2**.

$$2 \xrightarrow{k_{10}} \text{termination products} \qquad (10)$$

The rate law for peroxide decomposition would be that shown in the equation

$$-d[\text{Per}]/dt = k_1[\text{Per}] + k_7(k_1/2k_{12})^{1/2}[\text{Per}]^{1/2} \qquad (11)$$

Likewise, if both steps of the chain sequence proceed with equal facility, the steady-state concentration of the two chain-carrying radicals would be comparable and the cross-termination process would be operative.

$$2 + (\text{CH}_3)_3\text{CO}\cdot \xrightarrow{k_{12}} \text{termination products} \qquad (12)$$

The rate law for the peroxide decomposition would be that shown in the equation

$$-d[\text{Per}]/dt = k_1[\text{Per}] + (k_1k_6k_7/k_{12})^{1/2}[\text{Per}] \qquad (13)$$

Finally, if the hydrogen abstraction from **1** by the *tert*-butoxyl radical (eq 6) is rate limiting, termination would involve a bimolecular interaction of two *tert*-butoxyl radicals,

$$2\ (\text{CH}_3)_3\text{CO}\cdot \xrightarrow{k_{14}} \text{termination products} \qquad (14)$$

and the rate law is

$$-d[\text{Per}]/dt = k_1[\text{Per}] + k_6(k_1/2k_{14})^{1/2}[\text{Per}]^{3/2} \qquad (15)$$

Interestingly, the rate data for the decomposition of **1** in neither cumene nor *tert*-butylbenzene show strictly first-order dependency for the peroxide. The deviation observed in a first-order plot of the rate data for the decomposition of peroxide in cumene is less pronounced than it is in *tert*-butylbenzene.

Subjecting the rate data in Table I to a curve-fitting procedure[6] that indicates the kinetic order of a component shows a "best-fit" for the rate law (eq 16) for the reaction in cumene ($k_{\text{obsd}} = 2.32 \times 10^{-3}$; stand dev = 0.10×10^{-4}).

$$-d[\text{Per}]/dt = k_{\text{obsd}}[\text{Per}]^{1.1} \qquad (16)$$

Similar treatment of the rate data for the decomposition of **1** in *tert*-butylbenzene indicates the rate law (eq 17) for the decomposition reaction ($k_{\text{obsd}} = 4.65 \times 10^{-3}$; stand dev = 0.10×10^{-3}).

$$-d[\text{Per}]/dt = k_{\text{obsd}}[\text{Per}]^{1.4} \qquad (17)$$

Finding kinetic orders for the peroxide greater than unity indicate that the rate law (eq 15) is operative for the decomposition of the peroxides. Further, the observed kinetic orders for the peroxide reflect the contributions of the induced decomposition to the overall decomposition rates and the observed rate laws support the conclusion based on the product analysis, namely that the induced decomposition is more extensive in *tert*-butylbenzene than in cumene.

Experimental Section

Isopropyl *tert*-Butyl Peroxide. This material was prepared in the following manner using the general method described by Dickey and Bell.[7] A mixture of potassium *tert*-butyl peroxide (128 g, 1 mol) and isopropyl bromide (160 g, 1.3 mol) in 120 mL of isopropyl alcohol was stirred at room temperature for 1 week. The reaction mixture was poured into 4 L of water and the resulting organic layer was separated, washed several times with water, dried over anhydrous Na_2SO_4, and distilled. The isopropyl *tert*-butyl peroxide (26.4 g, 20% of theory) distilled at 36 °C at 70 mm. The NMR spectrum of the material showed a doublet centered at 1.19 ppm and singlet at 1.25 ppm (total, 15 H) and a heptet centered at 4.10 ppm (1 H).

Peroxide Decomposition Products Analysis. Solutions of isopropyl *tert*-butyl peroxide in *tert*-butylbenzene and in cumene (1:5 molar ratio of peroxide to solute) were placed in sealed glass tubes and heated at 135 °C in an oil bath. Tubes were removed at the time intervals designated in Table I and cooled to room temperature, and an accurately weighed portion of the reaction mixture was mixed with an accurately weighed amount of isoamyl acetate. The latter served as an internal standard for the gas chromatographic (10 ft × ¼ in. column packed with dodecyl phthalate on Chromosorb W) analysis of the unreacted peroxide and the reaction products acetone, isopropyl alcohol, and *tert*-butyl alcohol.

Registry No.—**1**, 15879-99-9; potassium *tert*-butyl peroxide, 14970-33-3; isopropyl bromide, 75-26-3; cumene, 98-82-8; *tert*-butylbenzene, 98-06-6; acetone, 67-64-1; isopropyl alcohol, 67-63-0; *tert*-butyl alcohol, 75-65-0.

References and Notes

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Reaction of Alkali Metal Cyanides with Alkyl Halides in HMPA or HMPA Containing Crown Ether

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Recently it was shown that potassium cyanide reacted with alkyl halides in benzene or acetonitrile containing crown ether to give high yields of alkyl cyanides.[1] We now wish to report the results of studies dealing with the reaction of sodium or potassium cyanide with alkyl halides in hexamethylphosphoramide (HMPA) in the presence or absence of 18-crown-6. The results show that sodium cyanide reacts rapidly with alkyl halides in HMPA even at room temperature with no crown ether present, that sodium cyanide reacts much faster with alkyl halides than potassium cyanide when no crown ether is present, and that even in a very polar aprotic solvent such as HMPA crown ether can increase the rate of reaction.

Reaction of sodium cyanide with alkyl halides in HMPA at room temperature with no crown ether present gave high yields of alkyl cyanides as shown in Table I. Isocyanides were not observed. Although the reactions shown in Table I were allowed to proceed for 24 h, the time required for complete reaction of the alkyl halide was usually much less. For example, 1-bromohexane completely reacted with sodium cyanide (1.5 mol equiv) in less than 1 h at room temperature. Also both 1-chlorohexane and 2-bromooctane reacted with sodium cy-