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

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

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.

$$2 + (CH_3)_3CO\cdot \xrightarrow{k_{12}} \text{termination products} \qquad (12)$$

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

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

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,

$$2\ (CH_3)_3CO\cdot \xrightarrow{k_{14}} \text{termination products} \qquad (14)$$

and the rate law is

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

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 ($k_{\mathrm{obsd}} = 2.32 \times 10^{-3}$; stand dev $= 0.10 \times 10^{-4}$).

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

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

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

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 × 1/4 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.

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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-

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Table I. Reaction of Alkyl Halides with Sodium Cyanide[f] in HMPA[a,g]

Halide	Registry no.	Products	% yield[b]
1-Bromohexane	111-25-1	1-Cyanohexane	98
1-Chlorohexane	544-10-5	1-Cyanohexane	96
1-Bromodecane	112-29-8	1-Cyanodecane	96
2-Chlorooctane	628-61-5	2-Cyanooctane	87[c]
		1- and 2-octenes	8
2-Bromooctane	557-35-7	2-Cyanooctane	84
		1- and 2-octenes	11
2-Iodooctane	557-36-8	2-Cyanooctane	59
		1- and 2-octenes	27
Cyclopentyl bromide	137-43-9	Cyclopentyl cyanide	65
		cyclopentene	*d*
Cyclohexyl bromide	108-85-0	Cyclohexyl cyanide	3
		cyclohexene	*d*
o-Dichlorobenzene		No reaction[e]	

[a] All reaction mixtures were stirred for 24 h at room temperature except in the cases of 2-chlorooctane and *o*-dichlorobenzene. [b] Yields were determined by GLC. [c] The reaction mixture was heated at 80 °C for 30 h. [d] Yield of alkene was not determined; no starting material remained. [e] There was no reaction even after 72 h at 120 °C with 18-crown-6 present. [f] Registry no. 143-33-9. [g] Registry no. 680-31-9.

Table II. Reaction of Alkyl Halides with Sodium or Potassium Cyanide[d] in HMPA or HMPA Containing 18-Crown-6[a,e]

Reaction	Alkyl halide	Type of cyanide	18-Crown-6[b]	% yield of alkyl cyanide[c]
1	1-Bromohexane	NaCN	No	98
2	1-Chlorohexane	NaCN	No	70
3	1-Chlorohexane	NaCN	Yes	79
4	1-Chlorohexane	KCN	No	10
5	1-Chlorohexane	KCN	Yes	81
6	1-Bromohexane	KCN	Yes	65

[a] All reactions were stirred for 5.7 h at room temperature. In all reactions except for the first, this reaction time was insufficient for complete reaction of the alkyl halide. [b] In some reactions as indicated, 5 mmol of 18-crown-6 was also present. [c] Yields were determined by GLC. [d] Registry no. 151-50-8. [e] Registry no. 17455-13-9.

anide in less than 8 h. An exception was 2-chlorooctane which required a reaction time of 30 h at a higher temperature (80 °C). In contrast, Liotta and co-workers[1] found that reaction of 1-bromohexane and 2-chlorooctane with potassium cyanide (2 mol equiv) in acetonitrile at 83 °C with 18-crown-6 present required reaction times of 40 and 244 h, respectively.

High yields of alkyl cyanides were obtained even from some secondary alkyl halides. The 84% yield of 2-cyanooctane obtained from 2-bromooctane was higher than that reported by Liotta and co-workers.[1] The higher yield is most likely due to the lower reaction temperature which disfavors the competing elimination reaction. The 87% yield of 2-cyanooctane from 2-chlorooctane is equal to that reported by Starks[2] using a phase-transfer catalyst system and is the highest yield of alkyl cyanide obtained from a secondary halide by any procedure. The aryl halide, *o*-dichlorobenzene, failed to react with sodium cyanide even when heated at 120 °C for 72 h. Addition of 18-crown-6 had no effect. This result is in contrast to our previous report[3] where sodium methoxide reacted readily with *o*-dichlorobenzene under similar conditions to give a 78% yield of *o*-chloroanisole.

Reaction of alkyl halides with alkali metal cyanides under the same conditions except for changes in the type of metal cyanide used and the presence or absence of 18-crown-6 gave the results shown in Table II. The reaction time was the same in all runs and was insufficent for complete reaction except in the case of 1-bromohexane with sodium cyanide. Reaction of sodium cyanide with 1-chlorohexane was much faster than that of potassium cyanide when no crown ether was present (reactions 2 and 4). This is probably due to the fact that sodium cyanide is more soluble in HMPA than potassium cyanide. When crown ether was added to improve the solubility of the potassium cyanide, it reacted with 1-chlorohexane at about the same rate as sodium cyanide (reactions 3 and 5). Addition of crown ether also improved the reactivity of sodium cyanide (reactions 2 and 3) although not as dramatically as in the case of potassium cyanide. We have observed similar effects of crown ethers in the reactions of potassium salts of carboxylic acids with alkyl halides in HMPA.[4] Although sodium cyanide reacted much more rapidly with 1-bromohexane than 1-chlorohexane, potassium cyanide reacted with 1-bromohexane in the presence of crown ether more slowly than 1-chlorohexane (reactions 5 and 6). Although this observation is contrary to the normally accepted leaving group order, it does agree with the observations of Liotta and co-workers[1] for similar reactions in acetonitrile.

Experimental Section

General Procedure (Table I). A mixture of alkyl halide (20 mmol), ground sodium cyanide (1.47 g, 30 mmol), and 40 mL of HMPA in a flask equipped with a drying tube was magnetically stirred for 24 h at room temperature (~21 °C). The reaction mixture was then poured into 80 mL of water which was extracted with two 80-mL portions of ether. The combined ether extract was washed with three 20-mL portions of water, dried with anhydrous sodium sulfate, and evaporated under reduced pressure. The yield of alkyl cyanide was determined by analysis of the residual liquid by GLC (6 ft × 0.25 in. 10% SE-30 on 60–80 mesh Chromosorb W). Product purified by GLC gave an infrared spectrum and refractive index identical to that observed or reported for an authentic sample. In the case of 2-chlorooctane the reaction was performed as above except the reaction mixture was heated at 80 °C for 30 h in a flask equipped with a condenser and drying tube. In the case of *o*-dichlorobenzene the reaction mixture which included 1.32 g (5 mmol) of 18-crown-6 was heated at 120 °C for 72 h.

General Procedure (Table II). A mixture of alkyl halide (10 mmol), ground metal cyanide (16.6 mmol), 20 mL of HMPA, and in some cases 1.32 g (5 mmol) of 18-crown-6 was magnetically stirred in a flask equipped with a drying tube for 5.7 h at room temperature (~21 °C). The reaction mixture was then poured into 40 mL of water which is extracted with two 40-mL portions of ether. The combined ether extract was washed with three 10-mL portions of water, dried with anhydrous sodium sulfate, and evaporated under reduced pressure. The yield of alkyl cyanide was determined by analysis of the residual liquid by GLC (6 ft × 0.25 in. 10% SE-30, 100 °C). Product purified by GLC gave an infrared spectrum and refractive index identical to that of an authentic sample.

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(4) Reaction of potassium pivalate with *sec*-butyl bromide in HMPA at room temperature for 24 h gave an 83% yield of *sec*-butyl pivalate when no 18-crown-6 was present and a 90% yield when 18-crown-6 present. Reaction between potassium butyrate and cyclopentyl bromide gave a 58% yield of cyclopentyl butyrate with no 18-crown-6 present and an 85% yield with 18-crown-6 present. Neither potassium pivalate or butyrate were completely soluble in HMPA although potassium pivalate was more soluble than potassium butyrate.