Hydrogen Atom Abstraction by a Cumyloxy Radical

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It has been generally understood that the rates of hydrogen atom abstraction from liquid hydrocarbons increase in the sequence: primary, secondary, and tertiary. This order has been considered to be independent of the nature of the attacking species, and has been explained as being due to the strengths of the C–H bonds being broken. In the course of our investigation of the autoxidation of hydrocarbons in the liquid phase, the relative reactivities of a series of hydrocarbons toward cumyloxy radicals were measured in view of the fact that, although many data had been reported on the relative reactivities toward atoms and free radicals,1) the reactivities of a series of hydrocarbons toward cumyloxy radicals had not yet been obtained. Another purpose is to compare the reactivities (and selectivities) of cumyloxy and cumylperoxy radicals,*1 since there are no definite data on the reactivities of two oxy radicals with the same alkyl group, the hydrocarbon portion in the radical.

Dicumyl peroxide was chosen as the source of the cumyloxy radicals since its thermal decomposition had been studied in detail by Kharasch and his co-workers,2) and by Bailey and Godin.3) These authors showed that dicumyl peroxide decomposed by a strictly first-order non-chain mechanism up to almost completion, the rate-determining step being the breakdown of the peroxide into free alkoxy radicals.2,3) Kharasch and his co-workers2) used cumene, *t*-butylbenzene, diisopropylcarbinol, and dodecane as solvents, and found the rates of decomposition to be nearly independent of the solvents.

The decomposition products were reported to be cumyl alcohol, acetophenone, methane, and the dimer of the solvent hydrocarbon.2,3) In addition to these products, a small amount of α-methylstyrene was found to be formed. No ethane, acetone, or α,α-dimethylbenzyl methyl ether was detected.

The first step in the decomposition of dicumyl peroxide is the scission of the peroxidic bond to produce two cumyloxy radicals. This radical either abstracts a hydrogen atom from the solvent to form cumyl alcohol, or decomposes to acetophenone and a methyl radical. The absence of acetone in the product mixture shows that the fission of the cumyloxy radical occurs at the carbon-methyl bond and not at the carbon-phenyl bond; this is in agreement with thermochemical predictions4) that the elimination of a methyl group requires an enthalpy increase of 0.3 kcal/mol, while that of a phenyl group would require 8.0

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1) W. A. Pryor, "Free Radicals," McGraw-Hill Book Co., N. Y. (1966), p. 149.

[*1] The investigation of the cumylperoxy radical is now in progress in our laboratory.

2) M. S. Kharasch, A. Fono and W. Nudenberg, *J. Org. Chem.*, **16**, 105 (1951).

3) H. C. Bailey and G. W. Godin, *Trans. Faraday Soc.*, **52**, 68 (1956).

4) P. Gray and A. Williams, *Chem. Revs.*, **59**, 239 (1959).

Table 1. The products of the thermal decomposition of dicumyl peroxide[a)]
(140°C, [peroxide] = 1.00×10^{-3} mol)

Solvent	Products in mol×10^3			k_1/k_2	Relative k_1[b)]
	I+II	III	(I+II)/III		
Tetralin	1.58	0.295	5.35	0.728	1.9
Phenylcyclohexane	1.12	0.740	1.52	0.285	
p-Xylene	0.961	0.990	0.972	0.119	0.20
Ethylbenzene	0.833	0.990	0.843	0.103	0.51
Cumene	0.797	1.14	0.700[c)]	0.0972	1.00
Toluene	0.725	1.07	0.677	0.0721	0.24
Diphenylmethane	0.748	1.28	0.585	0.0922	0.48

a) All experiments were performed in duplicate.
b) Relative reactivities per active α-hydrogen relative to cumene.
c) The values of 0.71 and 0.74 are given in Refs. 2 and 3 respectively.

kcal/mol. The absence of both ethane and α,α-dimethylbenzyl methyl ether, and the formation of methane in an amount equimolar to acetophenone,[2,3)] show that most of the methyl radicals attack the solvent and abstract the hydrogen atom. α-Methylstyrene is expected to be produced by the dehydration of cumyl alcohol.[5,6)] The amount of α-methylstyrene formed was always less than 5% of the cumyl alcohol formed.

These observations lead to the following scheme for the decomposition of dicumyl peroxide in a hydrogen-donor solvent:

$$C_6H_5(CH_3)_2COOC(CH_3)_2C_6H_5 \rightarrow 2C_6H_5(CH_3)_2CO\cdot$$

$$C_6H_5(CH_3)_2CO\cdot + RH \xrightarrow{k_1} \underset{\text{I}}{C_6H_5(CH_3)_2COH} + R\cdot$$

$$C_6H_5(CH_3)_2COH \rightarrow \underset{\text{II}}{C_6H_5(CH_3)C{=}CH_2} + H_2O$$

$$C_6H_5(CH_3)_2CO\cdot \xrightarrow{k_2} \underset{\text{III}}{C_6H_5COCH_3} + CH_3\cdot$$

$$CH_3\cdot + RH \rightarrow CH_4 + R\cdot$$

$$R\cdot + R\cdot \rightarrow R{-}R$$

The rates of the formation of cumyl alcohol and acetophenone can be expressed as Eqs. (1) and (2) respectively:[*2]

$$\text{d(cumyl alcohol)}/\text{d}t = k_1[C_6H_5(CH_3)_2CO\cdot][RH] \tag{1}$$

$$\text{d(acetophenone)}/\text{d}t = k_2[C_6H_5(CH_3)_2CO\cdot] \tag{2}$$

Hence,

$$\text{cumyl alcohol/acetophenone} = k_1[RH]/k_2 \tag{3}$$

Since k_2 may well be assumed to be constant in aromatic hydrocarbon solvents[*3] and since [RH] is known, the relative k_1 value can be measured on the basis of the knowledge of the amounts of cumyl alcohol and acetophenone formed.

The products obtained in eight solvents are shown in Table 1.

More than 90% of the initial peroxide was accounted for. The relative reactivities of the hydrocarbons toward cumyloxy radicals are also shown in Table 1. As Table 1 shows, toward the cumyloxy radical, the normal order of hydrogen reactivity, namely, primary<secondary<tertiary, is followed in the series of *p*-xylene, toluene<ethylbenzene, diphenylmethane<cumene. However, the secondary hydrogen atom of tetralin is much more reactive than that of cumene. The steric effect may be one of the reasons why cumene is less reactive than tetralin, since the α-hydrogen of cumene is rather hindered by two methyl groups. Another possibility is that, although the β-hydrogens of tetralin are not benzylic and although the derived radical can not be stabilized by resonance, the β-hydrogen atoms as well as the β-hydrogens may also be abstracted by the cumyloxy radical, since the *t*-butoxy radical abstracts hydrogen from cyclohexane more readily than from toluene.[7,8)]

Phenylcyclohexane has one tertiary and ten secondary hydrogen atoms. For the same reason as has been given above, the secondary hydrogens must also be abstracted by the cumyloxy radical; all the more, then, is the tertiary hydrogen in

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5) P. Gray and M. J. Pearson, *J. Chem. Soc.*, **1964**, 5725.

6) W. G. Lloyd, R. G. Zimmerman and A. J. Dietzler, *Ind. Eng. Chem., P. R. D.*, **5**, 326 (1966).

[*2] In this paper, the amount of cumyl alcohol formed was taken as the sum of cumyl alcohol and α-methylstyrene found.

[*3] It has been known that the reactions of alkoxy radicals, especially the k_2 values, are influenced by the solvents. (E. S. Huyser, "Advances in Free-Radical Chemistry," Vol. I, Logos Press, London (1965), p. 103.) However, in similar alkyl aromatic hydrocarbon media k_2 may well be assumed to be constant.

7) C. Walling and B. B. Jacknow, *J. Am. Chem. Soc.*, **82**, 6108 (1960).

8) P. Wagner and C. Walling, *ibid.*, **87**, 5179 (1965).

phenylcyclohexane hindered by phenyl and cyclohexyl groups.

Experimental

Dicumyl peroxide was obtained from the Nippon Oils and Fats Co. and had a purity of 99.3%. Tetralin, cumene, ethylbenzene, *p*-xylene, and toluene were shaken successively with sulfuric acid, water, sodium hydroxide, and water, dried with calcium chloride, and then distilled under a reduced pressure of nitrogen. Diphenylmethane and phenylcyclohexane were fractionally distilled. All the solvents were passed through an activated alumina column immediately before use.

Decompositions were carried out in a sealed flask equipped with a condenser, a sample inlet, and two side arms. An aliquot of the solution of dicumyl peroxide was introduced into the reaction vessel, the concentration of the peroxide being maintained at 0.200 mol/*l*. The reaction mixture was degassed under a vacuum through one side arm, while through the other nitrogen was introduced. This procedure was repeated four times. The vessel was then immersed to an oil bath thermostated at 140±0.5°C, and the reaction mixture was stirred by means of a magnetic stirrer.

Acetophenone, cumyl alcohol, and α-methylstyrene were determined by gas-liquid chromatography; Polyethylene Glycol 6000 column, at 170°C and with helium carrier gas. Methane and ethane were analyzed by glc; Molecular Sieve-13X, 30°C, He carrier gas. It was found that methane was the only gaseous product. The injection of an initial solution of dicumyl peroxide to glc gave peaks of both acetophenone and cumyl alcohol. In order to avoid this interference, dicumyl peroxide was decomposed almost completely. The injection of cumyl alcohol did not give any other peak, indicating that the decomposition of cumyl alcohol in the glc was negligible.