Mechanism of the Reaction of Cumyloxyl Radicals in a Mixture of Hydrocarbons

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Decay reactions of cumyloxyl radicals have been studied in a mixture of cyclohexane and aromatic hydrocarbon. The hydrogen transfer from solvent to oxyl radical increases considerably when small amounts of the aromatic hydrocarbon are present. The addition of cyclohexyl radical to the aromatic ring plays a decisive role in the mechanism of this reaction.

CUMYLOXYL radicals decay in non-polar media both by reaction with a solvent giving cumyl alcohol (CA) and by monomolecular fragmentation yielding acetophenone (APh) and methyl radical [reactions (1) and (2)].

$$\mathrm{PhC(CH_3)_2O\cdot + SH \xrightarrow{k_t} PhC(CH_3)_2OH + S\cdot} \qquad (1)$$

$$\mathrm{PhC(CH_3)_2O\cdot \xrightarrow{k_f} PhC(CH_3){=}O + \cdot CH_3} \qquad (2)$$

Generally we can assume that reaction (2) is not affected by the medium and its rate is a function of temperature only.[1] The ratio between alcohol and ketone formed is proportional to the rate of hydrogen abstraction from the solvent and expresses the relative reactivity of the medium hydrogens at a given temperature according to relation (3).[2] For a mixture of two

$$[\mathrm{CA}]/[\mathrm{APh}] = k_{\mathrm{t}}[\mathrm{SH}]/k_{\mathrm{f}} \qquad (3)$$

substances, the reactivity is additive and for the reaction of cumyloxyl radicals equation (4) holds.[2]

$$[\mathrm{CA}]/[\mathrm{APh}] = (k_{\mathrm{tA}}[\mathrm{S_AH}] + k_{\mathrm{tB}}[\mathrm{S_BH}])/k_{\mathrm{f}} \qquad (4)$$

Many experimental systems demonstrate the additivity of the reactivity of the components of mixtures. However, numerous deviations have also been observed *e.g.* in peroxide decomposition,[2] radical polymerization,[3] and radical reactions of polymers [4] in solvent mixtures.

A significant deviation from additivity was observed by Rado *et al.*[2] in a relatively simple system, namely cumyl peroxide decomposition in cyclohexane–toluene. Upon adding a small amount of toluene (*ca.* 1—2% v/v) the ratio [CA]/[APh] increases considerably with respect to the values for pure solvents. The formation of a complex is assumed to be the reason for this phenomenon; no conclusions were drawn concerning the nature of the complex and the mechanism of the process. Since hydrogen transfer plays a significant role in many radical processes, we searched for the reason for the observed apparent increase in the reactivity of the mixture of two hydrocarbons.

EXPERIMENTAL

Cumyl peroxide (Perkadox SB) was recrystallized from supercooled ethanol. Hydrocarbons used as reaction media were of analytical grade and were used without further purification.

The decomposition of the peroxide was carried out in sealed ampoules under nitrogen in an oil-bath for 10 half-lives of peroxide decomposition at a given temperature. The initial concentration of peroxide was in all cases 0.1M.

The amount of cumyl alcohol and acetophenone formed was determined by g.l.c. at 140 °C on a 150 cm column filled with 15% neopentyl glycol sebacate on WAW Chromosorb.

Qualitative analysis of other products was performed by g.l.c.–m.s. using JEOL JMS-D 100 and JGC-20K apparatus. The separation was carried out on the same column under the conditions given above. The mass spectrometer operated at an ionizing chamber temperature of 150—180 °C with emission of ionizing electrons at 100 A with an energy of 75 eV.

RESULTS AND DISCUSSION

The interaction of solvent-derived radical with the aromatic ring seems to be the most probable reason for the assumed complex formation. Thus we followed the formation of cumyl alcohol and acetophenone in mixtures of different hydrocarbons with aromatic compounds. As Figure 1 shows, the dependence of [CA]/[APh] *versus* the solvent composition in heptane–toluene and 2,2,4-trimethylpentane–benzene corresponds to equation (4); no extremes were observed in mixtures of toluene with n-butanol or decalin though some deviation here is obvious. However, this may be due to a physical reason, *e.g.* different solvation of the radicals with the components of the mixture. Moreover, in the case of n-butanol, the mechanism of the reaction of cumyloxyl radicals is more complex. This is confirmed by the fact that the sum [CA] + [APh] increases linearly with decreasing content of alcohol from 0.12M in pure butanol up to theoretical value of 0.20M in pure toluene

Since toluene does not produce extreme values of the [CA]/[APh] ratio in a mixture with any of the hydrocarbons, we studied the reaction in mixtures of cyclohexane and some aromatic solvents (Figure 2). In all cases a maximum was observed for the plot of [CA]/[APh] *versus* solvent composition at 5—10 mol % of aromatic hydrocarbon. In all cases, except for the mixture of toluene and butanol, the cumyloxyl radicals were converted quantitatively into alcohol and ketone as confirmed by the sum [CA] + [APh] which was determined to be 0.2 ± 0.01M.

To interpret the mechanism of the decay of cumyloxyl radical in a mixture of cyclohexane and aromatic compound, secondary reaction products were analysed qualitatively by the g.l.c.–m.s. method in cyclohexane–toluene, cyclohexane–nitrobenzene, and cyclohexane–chlorobenzene (95 : 5 mol %). In all mixtures the products of recombination of solvent radicals were identified as cyclohexylcyclohexane or 1,2-diphenylethane in the presence of toluene. Further, cyclohexyl(methyl)benzene was found in toluene–cyclohexane, cyclohexyl(nitro)benzene in nitrobenzene–cyclohexane, and cyclohexylbenzene in the presence of chlorobenzene. The amount of these products formed by simple recombination of the medium radicals should be negligible because of a low rate of substitution by oxyl radicals of hydrogen atoms on the aromatic ring [5] giving a low concentration of substituted phenyl radicals. A much better explanation for the formation of the observed adducts is alkylation of the aromatic ring by cyclohexyl radicals as studied by Shelton and Uzelmeier [6] for photolysis of di-t-butyl peroxide in a mixture of cyclohexane and aromatic compound.

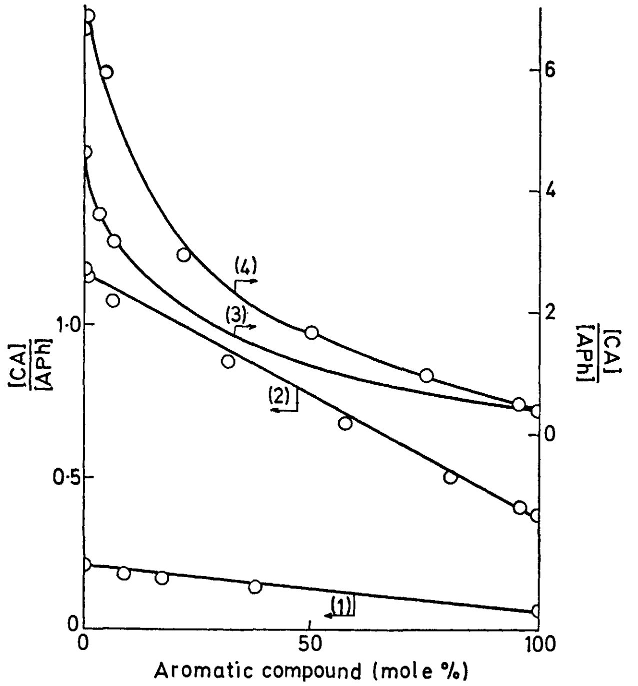

FIGURE 1 The ratio [CA]/[APh] *versus* solvent composition in benzene–2,2,4-trimethylpentane (1), toluene–heptane (2), toluene–decalin (3), toluene–butanol (4)

The first step in the supposed mechanism of the reaction of cumyloxyl radical in a mixture of cyclohexane and aromatic hydrocarbon is the formation of cyclohexyl radical by substitution. These radicals decay either by recombination or by reaction with the aromatic compound giving a relatively stable complex of cyclohexyl radical with the aromatic substrate with an extraordinarily reactive hydrogen. The simplest way to stabilize the complex is hydrogen abstraction by another radical. An increase in the cumyl alcohol content is observed when cumyloxyl radicals react with the complex radical. In the presence of chlorobenzene, the complex is more probably stabilized by splitting off the chlorine with methyl radical than by hydrogen abstraction with cumyloxyl radical. This is in line both with the formation of cyclohexylbenzene and with the fact that chlorobenzene in a mixture with cyclohexane gives the lowest maximum among all the aromatic compounds used.

As for quantitative differences in the height of the maxima for mixtures of toluene or ethylbenzene with cyclohexane, the difference almost disappears when the different reactivities of the two aromatic compounds in the pure state are taken into account. The significant effect of the nitro-group can be accounted for by the assumption that the reaction of cyclohexyl radical with the aromatic ring is a nucleophilic substitution and is activated by electronegative substituents. This assumption is supported by papers describing the nucleophilicity of secondary alkyl radicals in addition to the acryloyl group [7] and also by data [6] on the effect of the electronegative cyano-group which directs alkylation mainly to the *ortho-* and *para*-position, its effect on the reaction rate being strongly activating.

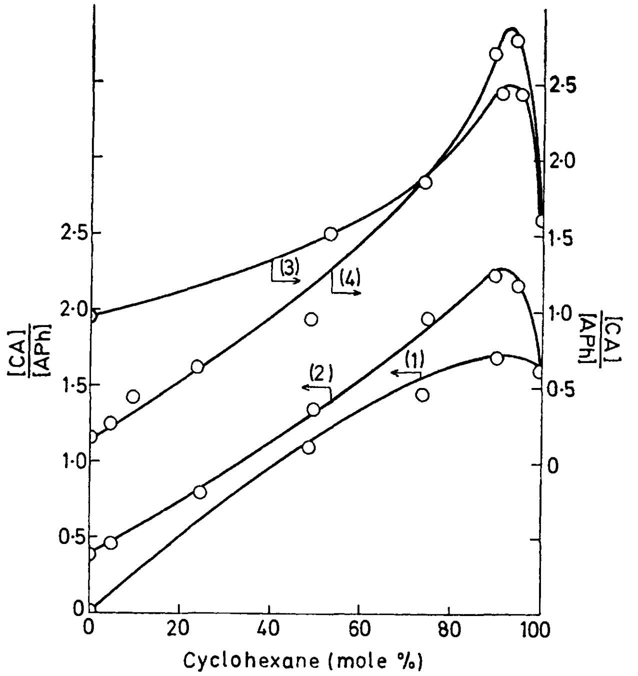

FIGURE 2 The dependence of [CA]/[APh] on the composition of cyclohexane mixed with chlorobenzene (1), toluene (2), ethylbenzene (3), and nitrobenzene (4)

The Scheme can be proposed for the reaction studied. If the rate of reaction (D) is assumed to be much higher than that of termination reactions (F), equation (5) holds for the ratio of the products formed. In the

$$[CA]/[APh] = 2k_2[S_1H]/k_1 + k_3[S_2H]/k_1 \qquad (5)$$

limiting case $[S_2H] \longrightarrow 0$ the ratio [CA]/[APh] may reach double the value of that in pure cyclohexane. In fact, the condition of the prevailing rate of reaction (D) is not valid at low concentrations of aromatic hydrocarbon because of low stationary concentration of radical complex. This assumption holds approximately at [S_2H] *ca.* 5—10 mol% when the maximum values for the ratio alcohol : ketone are observed.

$$\mathrm{RO\cdot} \xrightarrow{k_1} \mathrm{APh} + \cdot\mathrm{CH_3} \qquad \text{(A)}$$

$$\mathrm{RO\cdot} + \mathrm{S_1H} \xrightarrow{k_2} \mathrm{ROH} + \cdot\mathrm{S_1} \qquad \text{(B)}$$

$$\mathrm{RO\cdot} + \mathrm{S_2H} \xrightarrow{k_3} \mathrm{ROH} + \cdot\mathrm{S_2} \qquad \text{(C)}$$

$$\cdot\mathrm{S_1} + \mathrm{S_2H} \xrightarrow{k_4} \mathrm{K} \qquad \text{(D)}$$

$$\mathrm{RO\cdot} + \mathrm{K} \xrightarrow{k_5} \mathrm{ROH} + \text{products} \qquad \text{(E)}$$

$$2\mathrm{X\cdot}\ (\cdot\mathrm{S_1},\ \cdot\mathrm{S_2},\ \cdot\mathrm{CH_3}) \xrightarrow{k_6} \text{products} \qquad \text{(F)}$$

SCHEME R = cumyl, S_1H = cyclohexane, S_2H = aromatic hydrocarbon

Figure 3 shows plots of [CA]/[APh] *versus* the composition of toluene–cyclohexane mixtures at various temperatures. All three plots are qualitatively identical, greater amounts of acetophenone being formed at higher temperatures as expected.[8] Quantitative changes are hardly observable in the range 145—175 °C (Table), indicating nearly equal activation energies for the competitive processes (D) and (F). If the tendency of the maximum of [CA]/[APh] to decrease with temperature is accepted, it can be interpreted as the lowering of the stationary level of transfer complex due to increased temperature.

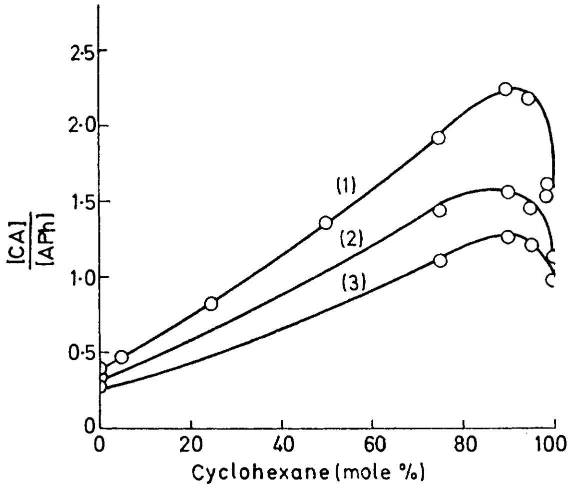

FIGURE 3 The ratio [CA]/[APh] *versus* the composition of toluene–cyclohexane mixtures at 145 (1), 160 (2), and 175 °C (3)

Of the hydrocarbons used, only cyclohexane exhibits a significant maximum for [CA]/[APh] in mixtures with aromatic compounds. Therefore the decay of cumyloxyl radicals was examined in mixtures of toluene with the similar hydrocarbons, cyclopentane and cyclohexanone. Figure 4 shows that the dependence of [CA]/[APh] on the composition of solvent with cyclopentane is the same as for cyclohexane while for cyclohexanone the maximum observed in the given region is not very pronounced. However, from the qualitative point of view we can predict a similar mechanism for both cases as for the mixture of aromatic compound with cyclohexane.

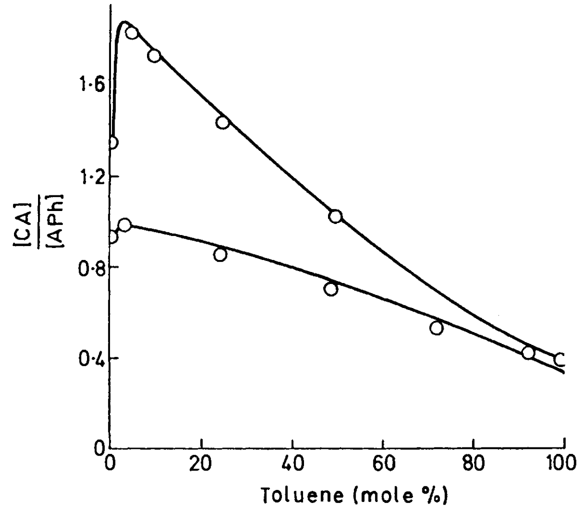

FIGURE 4 The dependence of [CA]/[APh] on the composition of toluene mixed with cyclopentane (1) and cyclohexanone (2)

Relative values of [CA]/[APh] in cyclohexane–toluene at three temperatures. [CA]/[APh] = 1 in pure cyclohexane at the given temperature

	Toluene (mol %)	
	5	10
t/°C	[CA]/[APh]	
145	1.35	1.39
160	1.28	1.38
175	1.25	1.30

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