Contribution to the Reactivity of Cumyloxy Radical
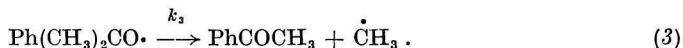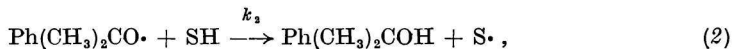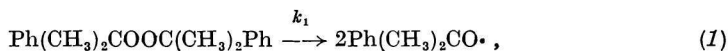
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In the present work the values of relative reactivity of the cumyloxy radical determined by chromatographic analysis of cumyl alcohol and acetophenone forming in cumyl peroxide decomposition in *n*-heptane, *n*-octane, isooctane, cyclohexane and toluene at the temperature of 145°C are shown. From the comparison of the values obtained with appropriate data for the *tert*-butoxy radical it results that the relative selectivity of the cumyloxy radical is 3 ± 1 times higher than that of *tert*-butoxy radical. The study of cumyloxy radical reactivity is completed by the phenomenon observed in its reaction with the mixture of paraffinic and aromatic hydrocarbons where, in view of their individual pure components, there occurs the deviation from the additivity of transfer constants.

By thermal decomposition of cumyl peroxide in hydrocarbon solvents the cumyloxy radicals are formed decaying partly by substitution reaction with the medium (SH) under formation of cumyl alcohol (CA) and partly by fragmentation producing acetophenone (APh) and methyl radicals

$$Ph(CH_3)_2COOC(CH_3)_2Ph \xrightarrow{k_1} 2Ph(CH_3)_2CO\cdot , \qquad (1)$$

$$Ph(CH_3)_2CO\cdot + SH \xrightarrow{k_2} Ph(CH_3)_2COH + S\cdot , \qquad (2)$$

$$Ph(CH_3)_2CO\cdot \xrightarrow{k_3} PhCOCH_3 + \dot{C}H_3 . \qquad (3)$$

Since the cumyl peroxide decomposition is of a severely unimolecular character [1] the ratio of rate constants of the processes (2) and (3) expressing, according to the scheme shown, the relation

$$\frac{k_2}{k_3} = \frac{[CA]}{[APh][SH]} \qquad (4)$$

may well be determined from the amount of both cumyl alcohol and acetophenone formed.

Here, the constant k_3 belongs to the unimolecular reaction of cumyloxy radical fragmentation and therefore its value, at a certain temperature, will not be dependent on the reaction medium. The ratios of constants k_2/k_3 then express directly the relation of the reactivity of various hydrocarbons in the process of the abstraction of hydrogen atoms by cumyloxy radicals. Thus the reactivity of various aliphatic, cycloparaffinic and aromatic hydrocarbons with respect to *tert*-butoxy ra-

dicals [2—4] and that of some polymers with respect to cumyloxy radicals [5—7] was determined.

Since cumyl peroxide has found at present lots of technical applications in the vulcanization of saturated polymers, we undertook to investigate the reactivity of thus produced radicals by which, along with the structure of hydrocarbon chain elements, the reaction mechanisms and, consequently, also the resulting character of the polymer transformation are determined. In the outcome study of this problem, decomposition products of cumyl peroxide in several hydrocarbons were determined and on the basis of k_2/k_3 values obtained according to relation (4) the selectivity of cumyloxy radicals in substitution reactions as a relation of the selectivity of once thoroughly investigated *tert*-butoxy radical standard was evaluated. This paper is supplemented also by the phenomenon observed in the reaction of cumyloxy radical with the mixture of aliphatic and aromatic hydrocarbons where the deviation from the additivity of these constants with respect to the individual pure components takes place.

Experimental

Cumyloxy radical reactivity was determined by chromatographic analysis of both cumyl alcohol and acetophenone formed by the peroxide decomposition in *n*-heptane, *n*-octane, isooctane, cyclohexane and toluene at the temperature of 145°C.

Before their application, toluene, *n*-heptane, *n*-octane and isooctane were purified by shaking for 12 hours with concentrated sulfuric acid (to remove olefins) and then, by diluted sodium hydroxide and distilled water to neutral reaction. In purifying cyclohexane we proceeded in a similar way but instead of sulfuric acid the nitration mixture was used by which benzene possibly present gets nitrated and nitrobenzene thus formed is reduced by addition of tin dichloride. All of the hydrocarbons were then dried for two days over calcium chloride and rectified on a column with an efficiency of about 120 theoretical plates at a reflux of 1 : 5.

Cumyl peroxide (Perkadox SB), used in these experiments, was purified by two-fold recrystallization from supercooled ethanol.

The proper experiments were performed in glass test tubes containing 1—3% cumyl peroxide solution in a corresponding solvent. After rinsing the glass tube contents by nitrogen (purified by routine technique) and cooling down to the temperature of —70°C the tubes were sealed in nitrogen atmosphere and annealed in an oil bath for 4 hours at the temperature of 145 ±0.7°C.

Cumyl alcohol and acetophenone formed by the cumyl peroxide decomposition under present conditions were determined by the method of gas—liquid chromatography at the temperature of 140°C. With the exception of *n*-octane, a 150-cm column filled with 15% of neopentyl glycol sebacate on W AW Chromosorb was used to separate the compounds analyzed. The accuracy of results obtained in this analysis was within the range of ±5% of the average value. In the case of *n*-octane another (80 cm long) column filled with 10% of ethylene glycol adipate on BLK Rysorb had to be used for the cumyl alcohol and acetophenone separation. Thus the divergence of analysis results increased to ±8%. Since in cyclohexane acetophenone could not have been separated quantitatively by either of the two procedures mentioned we confined to the determination of cumyl alcohol; acetophenone was calculated with respect to the peroxide concentration used owing to which the divergence of the resulting constant increased to ±15%. We proceeded similarly also in the mixtures of cyclohexane with toluene.

Results and Discussion

Since under experimental conditions cumyl peroxide practically completely decomposed, there may be expected, with respect to the mentioned scheme of its decomposition reaction, a 100% conversion of peroxide into cumyl alcohol and acetophenone. The results obtained do well satisfy this condition which for illustration we state for one case, that is to say, for the cumyl peroxide decomposition in isooctane (Fig. 1). But in addition to equimolarity of the original peroxide as well as of both its reaction products there may be found, in agreement with the reactions (1) and (3) of the scheme shown, also the linear relation between the concentration either of cumyl alcohol or acetophenone and cumyl peroxide concentration used (Fig. 2).
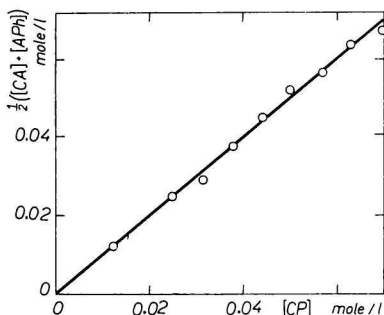

Fig. 1. The half of the sum of moles of determined cumyl alcohol and acetophenone *vs.* cumyl peroxide concentration after its 4 hours' decomposition in isooctane at temperature 145°C. (Points denote experimental values and the straight line the theoretically expected course.)
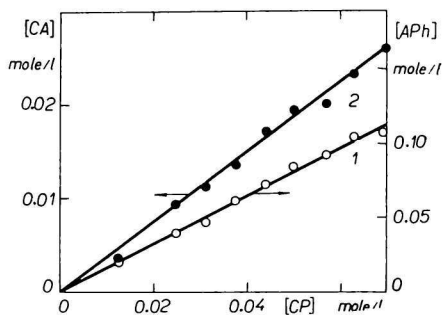
Fig. 2. The course of the formation of acetophenone (1) and cumyl alcohol (2) in dependence on cumyl peroxide concentration in isooctane after 4 hours' reaction at temperature 145°C.

It follows from the shown facts that out of the determined amount of cumyl alcohol and acetophenone produced by cumyl peroxide decomposition there may be attained, according to relation (4), the expression of relative reactivity of hydrocarbons with respect to cumyloxy radicals. The values of k_2/k_3 constants obtained by the procedure described in the five hydrocarbons investigated are presented in Table 1.

To evaluate the results obtained let us now compare the analogous data of another very reactive oxyradical of similar structure, namely *tert*-butoxy radical determined at the temperature of 135°C [2—4]. In Table 2 the reactivity data concerning both radicals compared are shown in relative units with respect to five hydrocarbons investigated.

Just a glance at the data given in Table 2 suggests that *tert*-butoxy radical is more reactive than cumyloxy radical. This is partly due to higher relative reactivity of *tert*-butoxy radical toward the same hydrocarbon, partly also to its lower relative selectivity with respect to various hydrocarbons with hydrogen atoms

Table 1

Relative reactivity of some hydrocarbons with respect to cumyloxy radicals at temperature 145°C

Hydrocarbon	k_2/k_3 [kg/mole]
isooctane	0.027
toluene	0.032
n-heptane	0.098
cyclohexane	0.132
n-octane	0.133

Table 2

Relative reactivity of cumyloxy and *tert*-butoxy radicals with respect to the investigated hydrocarbons

Hydrocarbon	Relative reactivity	
	cumyloxy radical at 145°C	*tert*-butoxy radical at 135°C
isooctane	1.00	4.48
toluene	1.18	5.63
n-heptane	3.63	6.00
n-octane	4.93	7.12
cyclohexane	4.88	8.18

Dimension kg/mole of k_2/k_3 constant was used to avoid the determination of densities of hydrocarbons at temperature 145°C (over boiling points) or inaccuracies which might well occur at extrapolation of the tabled values to this temperature.

of different reactivity. The fact evaluated may be seen, however, more vividly from the semi-quantitative analysis of the values shown in Table 2. This analysis is based on knowledge according to which there is a linear relationship between the logarithm of the rate constant ratio of the reaction of radical of certain type (R_1) with one (A) and the other substrate (B) and logarithm of such a relation with the radical of quite different type (R_2) [8]

$$\log \frac{k_{R_1A}}{k_{R_1B}} = n \log \frac{k_{R_2A}}{k_{R_2B}}. \tag{5}$$

Here the constant n expresses relative selectivity of mutually comparable radicals. Graphically, the solution of this relation for experimental data from Table 2 is shown in Fig. 3. According to this the relative selectivity of cumyloxy radical with regard to *tert*-butoxy radical is $n = 3 \pm 1$. (The numerical value of n was calculated by the method of least squares.) The nonsignificant difference of both temperatures (10 deg), at which the reactivity of both radicals has been determined, cannot affect the result considerably. Higher cumyloxy radical selectivity compared with *tert*-butoxy radicals may be attributed partly to the stabilizing effect of phenyl substituent, partly also to the steric hindrances of a more bulky radical in substitution reactions.

The process described enables the evaluation of cumyloxy radical reactivity in substitution reactions with hydrocarbons. Starting from the validity of the mentioned scheme of radical processes confirmed by the results obtained (see Figs. 1 and 2), the ratio of cumyl alcohol and acetophenone formed by the cumyl peroxide decomposition in the mixture of two hydrocarbons should conform to the relation

$$\frac{[CA]}{[APh]} = \frac{k_2}{k_3} [SH_1] + \frac{k_2'}{k_3} [SH_2]. \tag{6}$$

Here k_2 and k_2' express the rate constant of cumyloxy radical reaction with one (SH_1) and the other (SH_2) hydrocarbon component. The results obtained for the mixture

of cyclohexane with toluene (Fig. 4) do not, however, conform to this condition. By addition of toluene to cyclohexane the investigated ratio of alcohol and ketone does not only fail to decrease owing to the increase of less reactive component but even grows rapidly starting to decrease gradually after attaining about the 1.5
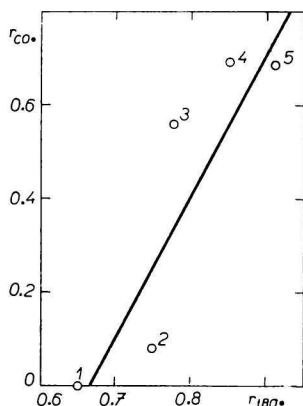

Fig. 3. Logarithm of relative reactivity of cumyloxy radical ($r_{CO\cdot}$) as the function of relative reactivity of *tert*-butoxy radical ($r_{tBO\cdot}$) with respect to isooctane (*1*), toluene (*2*), *n*-heptane (*3*), *n*-octane (*4*) and cyclohexane (*5*).
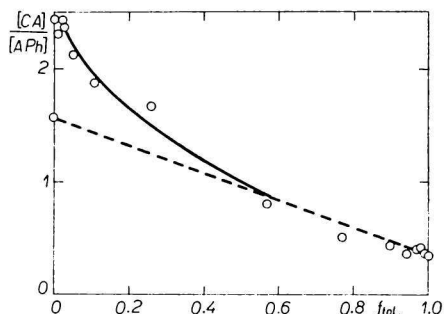
Fig. 4. Dependence of molar ratio of cumyl alcohol and acetophenone on the molar fraction of toluene in its mixture with cyclohexane (f_{tol}) after 4 hours' decomposition of cumyl peroxide (at the concentration of 0.04 mole/kg) at 145°C.

fold of the value of pure cyclohexane; approximately at the equimolar ratio of both hydrocarbons it continues practically in agreement with the relation (*6*). This character of the course of transfer reaction in mixture of the solvents is suggested right from the results of the degradation of polyisobutylene in solution initiated by cumyl peroxide [9].

A similar phenomenon of additivity deviation of transfer constants in the mixture of aromatic and aliphatic hydrocarbons was also observed in methyl [10] and chlorine [11] radicals as well as in the methyl methacrylate polymerization in the solution of chloroform, and acetone [12]. In contrast to the fact found by the authors, there is, however, a contrary tendency of deviation because of the decrease of transfer constant occurring in all cases. The phenomenon is not accounted for in quite an equal way; everybody unites, however, in the formation of transition complexes, owing to which transfer process activity decreases.

There exist so far but a few results, according to which this phenomenon might more exactly be judged and all of them are, as to their character, only qualitative comparisons of a certain particularity. The very fact, however, that in just the same mixture of paraffinic and aromatic hydrocarbons one radical type is marked by the reactivity decrease and the other one by its increase suggests that, apart from the interaction of substrate components also transition reactions of the entire system, including the reacting radical, will undoubtedly play an important part.

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