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Abstract

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REACTIVITY OF HYDROCARBONS AND THEIR DERIVATIVES IN THE POLYRECOMBINATION REACTION

The abstraction of labile α-hydrogen atoms from alkylaromatic hydrocarbons, ketones, esters, and other compounds by active radicals $(CH_3)_3CO\cdot$ or $\cdot CH_3$ is the first step in the reaction for the synthesis of polymers by polyrecombination ([1]).

$$(CH_3)_3COOC(CH_3)_3 \xrightarrow{k_1} 2(CH_3)_3CO\cdot, \tag{1}$$

$$(CH_3)_3CO\cdot + RH \xrightarrow{k_2} (CH_3)_3COH + R\cdot, \tag{2}$$

$$(CH_3)_3CO\cdot \xrightarrow{k_3} (CH_3)_2CO + \cdot CH_3. \tag{3}$$

The reactivity of various hydrocarbons RH toward homolytic abstraction of hydrogen atoms is determined both by the polar factor, which affects the electron density of the C–H bond, and by the degree of stabilization of the radical R· that is formed ([2,3]).

The purpose of the present work was to determine the reactivity of certain compounds, to compare it with the tendency of these compounds to form polymers as a result of the polyrecombination reaction, and also to establish some kinetic characteristics of this reaction. A quantitative estimate of the relative reactivity of RH during hydrogen abstraction by the butoxy radical is based on comparison of the ratios k_2/k_3 for different compounds. At low peroxide concentrations (3-5%) these ratios can be determined from the concentrations of tert-butyl alcohol and acetone formed in the reaction ([4–6]):

$$\frac{[\text{tert.-butyl alcohol}]}{[\text{acetone}]} = \frac{k_2}{k_3}[\text{RH}].$$

The content of tert-butyl alcohol and acetone in the reaction products was determined in the present work by gas-liquid chromatography. The reaction of the compounds studied with tert-butyl peroxide (at a concentration of the latter of 1–3 mol. %) was carried out in sealed ampoules, after preliminary degassing in vacuum. The ampoules were kept in a thermostat at temperatures from 115 to 165° with intervals of 10° for a time corresponding to the half-life period of the peroxide at the given temperature.

Table 1 gives the experimental results and the calculated ratios k_2/k_3 for various compounds at the maximum temperature of 165°. The values of k_2/k_3 were recalculated relative to diphenyl, whose reactivity was taken as unity. The table also gives the molecular weights of polymers obtained for some of the compounds studied by the polyrecombination reaction.

The change in relative reactivity agrees with existing concepts ([2,3,7]) concerning the competing or coincident influence of the polar factor and resonance stabilization on the reaction of abstraction of α-hydrogen atoms by radicals. Thus, the greatest reactivity of n-allylanisole in comparison with other compounds is apparently due to the coincident action of both factors. The presence of an electron-donating methoxy group leads to an increase in the electron density on the α-CH_2 group owing to the predominant influence of the electromeric

Table 1

Relative reactivity of various compounds in the reaction of abstraction of an α-hydrogen atom at a temperature of 165°

Compounds	$[RH]$, mol/l	Molar ratio tert.-butyl alcohol/acetone	k_2/k_3	k_2/k_2 relative to diphenyl	Maximum molecular weight of polymers obtained in the polyrecombination reaction
p-$CH_3O{-}C_6H_4{-}CH_2{-}CH{=}CH_2$	6.45	7.84	1.121	86.3	$5 \cdot 10^6$
p-$CH_3{-}C_6H_4{-}CH_2{-}CH{=}CH_2$	6.58	3.48	0.529	40.7	$1 \cdot 10^6$
$C_6H_5{-}CH_2{-}CH{=}CH_2$	7.55	3.51	0.465	35.8	—*
p-$H{-}C(CH_3)_2{-}C_6H_4{-}C(CH_3)_2{-}H$	5.23	2.68	0.523	40.2	$9.8 \cdot 10^5$
$C_6H_5{-}CH_2{-}C_6H_5$	5.93	1.35	0.228	17.5	$1 \cdot 10^6$
p-$CH_3{-}C_6H_4{-}CH_3$	8.04	1.13	0.142	10.9	$1.7 \cdot 10^5$ **
$C_6H_5{-}CH_2{-}O{-}C(O){-}C_6H_5$	5.24	0.507	0.097	7.53	$4 \cdot 10^5$
$C_6H_5{-}CH_2{-}C(O){-}C_6H_5$	7.41	0.695	0.094	7.25	$1 \cdot 10^5$
$C_6H_5{-}C(O){-}C_6H_5$	6.00	0.183	0.0305	2.34	$1.5 \cdot 10^3$

Compounds	$[RH]$, mol/l	Molar ratio tert.-butyl alcohol/acetone	k_2/k_3	k_2/k_2 relative to diphenyl	Maximum molecular weight of polymers obtained in the polyrecombination reaction
$C_6H_5-C_6H_5$	6.43	0.0835	0.013	1	$4 \cdot 10^3$
C_6H_5-CN	9.8	0.0946	0.0096	0.737	$1.4 \cdot 10^3$

* For the synthesis of the polymer, allylbenzene was not used because of its low boiling point.
** The polymer was obtained from 1,2-ditolylethane.

- E-effect, as compared with the inductive $-I$-effect, which should facilitate attack of this group by the electrophilic butoxyl radical ([8]). The increase in stability of the radical formed owing to conjugation of the unpaired p-electron with the π-electrons both of the benzene ring and of the vinyl group also facilitates abstraction of the α-hydrogen atom:

$$CH_3O-C_6H_4-CH_2-CH{=}CH_2 \xrightarrow{(CH_3)_3CO\cdot} CH_3O-C_6H_4-\dot{C}H-CH{=}CH_2 \leftrightarrow CH_3O-C_6H_4{=}CH-CH{=}CH_2$$

In the absence of a methoxy group, the influence of only one factor—stabilization by conjugation—leads, in the case of allylbenzene, to a decrease in the reactivity of the CH_2 group. The decrease in reactivity in the series p-diisopropylbenzene—diphenylmethane—p-xylene corresponds to the decrease, observed in many reactions, in the mobility of α-hydrogen atoms from tertiary to primary ([7]). Of the radicals of the benzyl type, the diphenylmethyl radical is the most stabilized by conjugation ([9]). However, p-diisopropylbenzene is more

more reactive than diphenylmethane, evidently as a result of the electron-donating properties of the methyl groups attached to the α-carbon atom. In the lower part of the table are the least reactive compounds, including those devoid of mobile α-hydrogen atoms. The reaction of the latter with tert-butyl peroxide is associated with the predominant decomposition of tert-butoxy radicals and subsequent methylation of the benzene rings ([10]). With substantial consumption of peroxide under the conditions of the polyrecombination reaction, these methylated derivatives may be incorporated into the polymer chain. From comparison of the molecular weights of the polymers obtained from the starting compounds by the polyrecombination reaction, it is seen that there is a definite correspondence between the molecular weight of the polymer and the reactivity of the starting compound in the first act of the reaction—the abstraction of hydrogen with formation of a radical of the starting compound.

Fig. 1. Logarithmic dependence of the ratio of tert-butyl alcohol to acetone on the reciprocal absolute temperature (in parentheses are the values of $E_2 = \Delta E$, kcal/mole, $\Delta E = 4.57 \text{ tg}\,\alpha$; $e = 5 \cdot 10^3$).
1—allylanisole; 2—allylbenzene; 3—allyltoluene; 4—*p*-diisopropylbenzene (4.3); 5 —*p*-cymene (5.8); 6—*p*-ditolylmethane (5.54); 7—*p*-xylene; 8—diphenylmethane (3.3); 9, 10—methyl ester of diphenylmethane-4-carboxylic acid and anisylbenzyl (about 5.95); 11—4-benzylpyridine (7.5); 12—benzyl methyl ketone; 13—benzyl benzoate (6.0); 14—diphenylethylene (4.3); 15—benzophenone (9.5); 16—diphenyl oxide (9.4); 17—benzonitrile (7.0); 18—diphenyl (9.9).

In Fig. 1 is shown the change in the dependence of k_2/k_3 (expressed as

$$\lg \frac{[\text{tert.-butyl alcohol}]}{[\text{acetone}]}$$

) on the absolute temperature for the compounds studied. The linear character of the dependence indicates that the rates of the hydrogen-abstraction reactions obey the Arrhenius equation. From the slope of the straight lines, ΔE—the difference in the activation energies of reactions (2) and (3)—was calculated. Using the known value of the activation energy of reaction 3—the decomposition of the butoxy radical, amounting to 15 kcal/mole ([11])—one can determine the absolute values of the activation energy of reaction (2), the abstraction of a hydrogen atom, E_2. For diphenylmethane,

$$E_2 = E_3 - \Delta E = 15 - 11.7 = 3.3$$

kcal/mole*. Since the activation energy of recombination of the radicals of the starting compounds is very small and in a number of cases close to zero ([7]), it is obvious that the reaction of hydrogen abstraction from the starting compound is the determining one for the entire process of chain growth by the polyrecombination reaction. For most compounds with mobile α-hydrogen atoms, the activation energy, as is seen from the data given, varies within the range 3-8 kcal/mole, i.e., within the same limits as the activation energy of the chain-growth reaction in polymerization ([7]).

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* The corresponding E_2 values for the other compounds are given under Fig. 1.

Note: Figure translations are in progress. See original paper for figures.