Chemistry

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Abstract

Full Text

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THE INFLUENCE OF POLAR FACTORS IN THE POLYRECOMBINATION REACTION

In work (^{1}) the activation energy was found for the reaction of abstraction of labile α-hydrogen atoms during the thermal decomposition of tert-butyl peroxide in various hydrocarbons and their derivatives, and it was shown that changes in the relative reactivity of these compounds are affected by the factor of resonance stabilization of the radicals formed.

The aim of the present work was a quantitative assessment of the influence of the polar factor on the reaction of homolytic abstraction of an α-hydrogen atom, which is the first step of the polyrecombination reaction, and on the recombination process of the radicals formed. The objects of the investigation were diphenylmethane derivatives with various electron-donating and electron-accepting substituents in the benzene rings.

The change, under the influence of these substituents, in the electron density at the C—H bonds of the reaction center (the α-methylene group) may be reflected in the rate of attack on this group by electrophilic radicals. Such a radical, according to Russell' s data (^{2}), close in polarity to the chlorine atom, proves to be the tert-butoxy radical.

The influence of polar factors in the reaction of this radical with the methyl group of toluenes substituted in the ring was established by Johnson and Williams (^{3}).

The reactions occurring during the decomposition of tert-butyl peroxide in the compounds investigated in the present work may be represented as follows:

$$(\mathrm{CH_3})_3\mathrm{COOC}(\mathrm{CH_3})_3 \xrightarrow{K_1} 2(\mathrm{CH_3})_3\mathrm{CO}\cdot, \tag{1}$$

$$(\mathrm{CH_3})_3\mathrm{CO}\cdot + \mathrm{XC_6H_4CH_2C_6H_4X} \xrightarrow{K_2} (\mathrm{CH_3})_3\mathrm{COH} + \mathrm{XC_6H_4\dot{C}HC_6H_4X}, \tag{2}$$

$$(\mathrm{CH_3})_3\mathrm{CO}\cdot \xrightarrow{K_3} (\mathrm{CH_3})_2\mathrm{CO} + \cdot\mathrm{CH_3}. \tag{3}$$

A measure for estimating the reactivity of various diphenylmethane derivatives in reaction (2) is the ratio of the rate constants of the reactions k_2/k_3, which, at low peroxide concentrations that preclude substantial formation of dimers, can be expressed through the ratio of the molar concentrations of tert-butyl alcohol and acetone (^{4}, ^{5})

$$\text{(tert-butyl alcohol)/acetone} = \frac{K_2}{K_3}(\text{RH}). \qquad (4)$$

The influence of the polar factors proper in changing the relative reactivity will be determined by the correspondence of these changes to the Hammett equation.

The ratio of tert-butyl alcohol to acetone in the reaction products was determined by the method of gas-liquid chromatography. The reaction was carried out in evacuated ampoules, in which the compounds under investigation, after addition of tert-butyl peroxide (5-6%), were kept at 140° for 6 hours. Since all these compounds had melting points considerably above 140°, a 30% solution of them in benzonitrile was used to carry out the reaction in a homogeneous medium. The latter, as special experiments showed, is completely inert to the action of tert-butoxy radi-

cals under the given conditions. However, during decomposition of these radicals in benzonitrile, methylation of the benzene ring occurs, whereas under the harsher conditions we studied (200°C and consumption of 2 mol of peroxide), polymers are formed from the methylation products (^6).

Table 1

Results of determining the dependence of the relative reactivity K_2/K_3 of the α-hydrogen atoms in diphenylmethane and tetraphenylethane on the polar properties of substituents with respect to the tert-BuO radical

Substituents* X: number	Substituents* X: structure of substituents X	σ (^7)** para	Diphenylmethane derivatives*** K_2/K_3	Diphenylmethane derivatives*** K_2/K_0	Diphenylmethane derivatives*** $\lg\frac{K_2}{K_0}$	Symmetric tetraphenylethane derivatives*** K_2/K_3	Symmetric tetraphenylethane derivatives*** K_2/K_0	Symmetric tetraphenylethane derivatives*** $\lg\frac{K_2}{K_0}$
2	OCH_3	$-0,536$	0,0943	1,152	0,0615	0,0930	1,282	0,1090
2	CH_3	$-0,340$	0,865	1,055	0,0233	–	–	–
–	–	0,0	0,0820	1,0	0,0	0,0730	1,0	0,0
1	$COOCH_3$	$+0,235$	0,0723	0,0882	$-0,0545$	0,0674	0,923	$-0,0348$
1	COOH	$+0,265$	0,0734	0,0897	$-0,0472$	0,0646	0,885	$-0,0531$
2	$COOCH_3$	$+0,470$	0,0685	0,0836	$-0,0778$	0,0579	0,793	$-0,1007$

Substituents X: number	Substituents* X: structure of substituents X	σ (^7)** para	Diphenylmethane derivatives*** K_2/K_3	Diphenylmethane derivatives*** K_2/K_0	Diphenylmethane derivatives*** $\lg \frac{K_2}{K_0}$	Symmetric tetraphenylethane derivatives*** K_2/K_3	Symmetric tetraphenylethane derivatives*** K_2/K_0	Symmetric tetraphenylethane derivatives*** $\lg \frac{K_2}{K_0}$
1	CN	$+0,628$	0,0654	0,797	$-0,0985$	0,0463	0,634	$-0,1979$
2	$COCH_3$	$+1,032$	0,0563	0,685	$-0,1645$	0,0337	0,462	$-0,3354$
2	CN	$+1,256$	0,0567	0,691	$-0,1605$	0,0447	0,653	$-0,1851$
2	NO_2	$+1,556$	0,0591	0,721	$-0,1421$	–	–	–

* All substituents are in the para position. When the substituents contained labile hydrogens, a correction was introduced into K_2/K_3. In symmetric tetraphenylethane, in determining K_2/K_3 for the hydrogen of the group $>$ C—H, only the substituents bonded to this group through the benzene nuclei were taken into account.

** In the case of two identical substituents, σ was doubled.

*** Solutions in benzonitrile containing 5.7% tert-butyl peroxide were used; temperature 140°C.

Table 1 gives the results of experiments determining the relative reactivity of a series of nucleus-substituted diphenylmethane derivatives, as well as the corresponding dimers, specially synthesized and used as starting compounds.

The reactivity data were obtained by referring the values K_2/K_3 (equation (4)) to the corresponding value for unsubstituted diphenylmethane and tetraphenylethane, whose reactivity was taken as unity, which leads to the desired ratio K_2/K_0 (where $K_0 = K_2/K_3$ for diphenylmethane and tetraphenylethylene).

Fig. 1

The change in relative reactivity, taken in the form $\lg(K_2/K_0)$ and plotted on the ordinate axis in Fig. 1, as a function of the constants σ characteristic of each of the substituents (^7), obeys, as is seen from the figure, the Hammett equation $\lg(K_2/K_0) = \rho\sigma$. The value of ρ, determined from the slope of the straight lines, is -0.15 for diphenylmethane derivatives (1) and -0.25 for the corresponding dimers (2).

From the data obtained it is seen that introduction of electron-acceptor substituents into the benzene ring leads to a decrease in the mobility of the α-hydrogen atoms, whereas electron-donor substituents increase the reactivity of these atoms with respect to the butoxyl radical, which agrees with the data of Johnson and Williams (^3). This may be

is explained by the corresponding change in the electron density on the C—H bond of the reaction center, for example, by its considerable decrease in the case of the dimethyl ester of 4,4-diphenylmethanedicarboxylic acid owing to the coincident action of the $-I$ and E effects caused by electron-acceptor substituents:

$$CH_3O-C(=O)-C_6H_4-\overset{+}{C}H_2-C_6H_4-C(=O)-OCH_3$$

For dimeric products, for example for the dimer of the ester of the same acid (tetraphenylethanetetracarboxylic acid), two carbomethoxy groups will correspond to one α-C—H bond; as a result, one may expect a twofold greater decrease in the electron density on this bond and an intensification of the polar effect in the reaction with the butoxy radical. Indeed, the value of ρ found for the dimers (-0.25) and for the corresponding diphenylmethane derivatives (-0.15) is consistent with a greater influence of the polar effect in the case of the dimers.

In another work ([8]) it was shown that, of all the compounds studied, when they are treated with tert-butyl peroxide in an equimolecular ratio, only oligomers are obtained, in contrast to diphenylmethane, which under the same conditions is converted into high-molecular-weight polydiphenylmethylene ([9]). The reason for this difference apparently lies in the fact that the radicals formed from diphenylmethane derivatives retain a certain polarity at the reaction center, expressed in a decrease or increase of the electron density on the α-carbon atom, depending on the nature of the substituent groups, as compared with the radical of unsubstituted diphenylmethane.

Thus, irrespective of the greater or lesser ease of the primary act of the reaction —the abstraction of the α-hydrogen atom from substituted diphenylmethanes— the subsequent recombination of these radicals is apparently hindered because of their distinctly polar character. This agrees with the observations of Dolgoplosk et al. ([10]), and also of Shelton and Henderson ([11]), on the preferential recombination of those radicals that differ significantly in degree of polarity, for example,

$$RO_2\cdot > RO\cdot \gg R\cdot$$

In this series the radical $R\cdot$ recombines preferentially with $RO_2\cdot$, in its absence with $RO\cdot$, and only in the absence of both is the dimer R—R formed ([11]).

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

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