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CORRELATION OF SUBSTITUENT RESONANCE EFFECTS WITH FREE RADICAL SPIN DENSITIES

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The rate constants of radical reactions are known to depend at least on three principal effects: polar, resonance and steric. A steric effect can be ignored for compounds which do not have bulky substituents. Then substituent effects can be expressed in terms of the Taft equation (1):

$$\lg(k_{sub}/k_o) = \rho^*\sigma^* + r^*\sigma^r \qquad /I/$$

(k_{sub} and k_o are rate constants of substituted and unsubstituted compounds respectively, σ^* and σ^r - polar and resonance substituent constants).

Previously we demonstrated (2) that chain transfer constants of the telomerization of ethylene with halomethanes C_n with $n \geqslant 3$ (corresponding to relative values of rate constants of the substitution reactions of $X(CH_2CH_2)_n\cdot$ radicals) and rate constants of methyl radicals with chlorobromomethanes (3) obey the Taft equation without the resonance term, i.e. that the resonance effect of halogen substituents in the reactions under consideration is insignificant. From these considerations $\rho^* = 2,33 \pm 0,04$, $C^{CH_4} = 1,5\cdot10^{-6}$ ($\sim$100°). Allowing for $\rho^* = r^* = 2,33$ one can find σ^r of substituents offering both the polar and resonance effect *).

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*) This assumption is valid because the variation of r^* influences only the absolute value of σ^r but does not affect the relative scale of resonance constants.

Results of calculation based on this assumption and on use of chain transfer constants of the ethylene telomerization are listed in Table.

Table

Resonance constants of substituents (σ^r) and unpaired spin densities (ρ_R)

R-X	$C_{\geq 3}$ (100°)	k/k_{CH_4} b) (100°)	$\sigma^*(I)$	σ^r	ρ_R	
CH_3-I	4,5		0	0	1,000	
CH_3CH_2-I	14,8		-0,10	0,32	0,919	(15)
$(CH_3)_2CH$-I	48,3		-0,20	0,64	0,844	(15)
CH_3-H	$1{,}5 \cdot 10^{-6}$	1	0	0	1,000	
$HOOCCH_2$-H	0,0037	78,9 c) (6)	1,05	0,40	0,923	(16)
CH_3-Br	0,0025		0	0	1,000	
$HOOCCH_2$-Br	3,7		1,05	0,31	0,923	(16)
$NCCH_2$-H	0,0283	474 (7)	1,3	0,54	0,852	(17)
$C_6H_5CH_2$-H	0,0254	610 d) (8) e) (9)	0,215	1,605	0,621 f)	
CH_3COCH_2-H	0,0290	346 d) (5,8,10,11)	1,12 f)	0,72 f)	0,830	(18)
CH_2=$CHCH_2$-H	0,015 a) (4)	700 d) (8,12)	0,1	1,62	0,604	(19)
$HOCH_2$-H	0,0021 a) (4)	121 d) (11,13)	0,555	0,795	0,840	(17)
CH_3OCH_2-H		326 d) (8,13,14)	0,520	0,973 f)	0,770	(20)

a) Chain transfer constants in the ethylene polymerization at 130° and 1360 atm. b) Ratio of methyl radical rate constants in the gas phase, (k_{CH_4} = 1900 $cm^3 mole^{-1} sec^{-1}$ at 100° (5)). c) A reaction with CH_3COOCD_3. d) The average value. e) All rate constants cited in this paper are recalculated taking into account the corrected value of rate constant of methyl radical recombination: $2{,}3 \cdot 10^{13}$ $cm^3 mole^{-1} sec^{-1}$ (21). f) Found with the aid of the equation /2/.

Now σ^r can be expected to be directly proportional to $1 - \rho_R$, (ρ_R is the unpaired spin density on the α-carbon atom of forming free radical). Indeed we found:

$$\sigma^{r} = (4{,}23 \pm 0{,}48)(1 - \rho_R) \qquad /2/$$

for R = CH_3, CH_3CH_2, $(CH_3)_2CH$, $CH_2{=}CHCH_2$, $HOCH_2$, $HOOCCH_2$, $NCCH_2$. Coefficient of correlation r = 0,988. Experimental ρ_R were calculated according to the most accurate modification of the McConnell equation for splitting constants of methyl group ($a^{H}_{CH_3}$) of radicals $CH_3\dot{C}HY$, (Y = H, CH_3, COOH, etc.), were used (15,22):

$$a^{H}_{CH_3} = 29{,}3(1-0{,}081)\rho_R \qquad /3/$$

$\sigma^{r}_{CH_2COCH_3}$, $\sigma^{r}_{CH_2OCH_3}$ and $\rho_{CH_2C_6H_5}$ were also determined by equation /2/, (see Table). Previously it was supposed (23) that $\sigma^{*}_{CH_2COCH_3}$ = 0,60 (1) is small for free radical reactions. With $\sigma^{r}_{CH_2COCH_3}$ = 0,72 the equation /1/ gives $\sigma^{*}_{CH_2COCH_3}$ = 1,12. The necessity of the modification is confirmed in the study of methyl radical rate constants in the gas phase.

Reactions of methyl radicals in the gas phase can be exemplified by an application of equation /1/ with σ^{*} and σ^{r} listed in Table to other free radical reactions. A substitution of rate constants of the hydrogen abstraction by methyl radicals in the gas phase at 100° in this equation gives $\rho^{*} = r^{*} = 1{,}51 \pm 0{,}12$.

In the present investigation all calculations were carried out without taking into account a statistical factor, because its interpretation in terms of the usual "intuitive" ideas does not in general coincide with absolute rate theory calculations (24). However it is noted that the inclusion of a statistical factor in equation /1/ does not significantly change the relations obtained. Thus the equation /2/ becomes:

$\sigma^{r} = (4{,}09 \pm 0{,}60)(1-\rho_R)$, with a coefficient of correlation r = 0,981.

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