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POLAR vs BDE EFFECTS ON ALDEHYDIC HYDROGEN ATOM TRANSFER REACTIONS OF BENZALDEHYDES[1] BY t-BUTOXY RADICALS

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Summary Aldehydic hydrogen atom abstractions from benzaldehydes by t-butoxy radicals from t-butylperoxide exhibit a Hammett rho of -0 32, which is better correlated with σ^+ than σ and rationalized in terms of the contribution of dipolar charge-separated transition state

Since Hammett equation was first applied to homolytic reactions by Walling and Mayo in the late forties[2], charge-separated dipolar transition states of hydrogen atom transfer reaction (HTR) of toluenes[1] have enjoyed long acceptance and explanation for the polar effect by the substituents (Polar effect)[3,4]

The concept of the polar effect was seriously challenged by Zavitsas et al in 1972[5] They suggested that the negative rho values hitherto observed in the reactions of the toluenes simply reflected the changes of ground-state benzylic C-H bond dissociation energies by the substituents (BDE effect)

Contrary to the predictions by the BDE effect, Pryor et al reported positive rho values in the reactions of the toluenes with t-butyl radical[6-8]

Recently, Jackson et al , in the thermolysis of $YC_6H_4CH_2$-Hg-$CH_2C_6H_4Y$, observed unusual rate acceleration with Y being para-substituents over the meta-ones, during which the transition states were presumed to assume partial benzyl radical character[10] We, accordingly, have scanned the data of HTR of toluenes[11-14] and have not noticed such deviations from Hammett correlation with the para-substituted toluenes This may be taken as an additional indication that the transition states are devoid of neutral benzyl radical character and, instead, have the dipolar structure

Presently, we have undertaken to study the mechanism of aldehydic hydrogen atom transfer reactions of benzaldehydes which has attracted only limited attention[15-17]

Reactions at 130°C and for fifty minutes of degassed and sealed Pyrex ampoules containing variable concentrations (0 05 - 0 15 M) of benzaldehydes with t-butylperoxide (TBP, 0 05 M) in benzene led to the formation of t-butyl alcohol and acetone in the following reactions The period of fifty minutes corresponds to approximately 20% decomposition of TBP

$$YC_6H_4CHO + (CH_3)_3CO \xrightarrow{k_a} YC_6H_4CO + (CH_3)_3C\text{-}OH \qquad (1)$$

$$(CH_3)_3CO \xrightarrow{k_d} CH_3 + CH_3COCH_3 \qquad (2)$$

Ratios of (t-butyl alcohol)/(acetone) were determined by g l c method[18] and were plotted as the function of the concentrations of each aldehydes to give excellent straight lines (correlation factors 0 990 ± 0 005)[19] The slopes of the lines correspond to the ratios of the rate constants (k_a/k_d) in the following equation and the results are shown in Table 1

$$\frac{[\text{t-BuOH}]}{[\text{CH}_3\text{COCH}_3]} = \frac{k_a}{k_d}\,[\text{YC}_6\text{H}_4\text{CHO}] \qquad (3)$$

Table 1 Relative Reactivities of Aldehydic Hydrogen of Benzaldehydes toward t-Butoxy Radical at 130°C

Substituents	k_a/k_d [a]		σ [b]	σ^+ [b]
p-CH_3	17 4 [c]	1 31	-0 17	-0 31
m-CH_3	13 5 [c]	1 02	-0 07 [d]	-0 07 [d]
H	13 3	(1)	0	0
p-Cl	11 8	0 89	0 23	0 11
p-Br	11 6	0 87	0 23	0 15
m-F	10 2	0 77	0 34	0 35
m-Cl	9 7	0 73	0 37	0 40
m-CF_3	9 2	0 69	0 43	0 52
m-CN	8 8	0 66	0 56	0 56

a Error limits are within ±5%, being the average deviations of three or more experiments
b C D Ritchie and W F Sager, Progr Phys Org Chem , 2, 334 (1964)
c Corrections were made for the hydrogen atom transfer from the methyl groups
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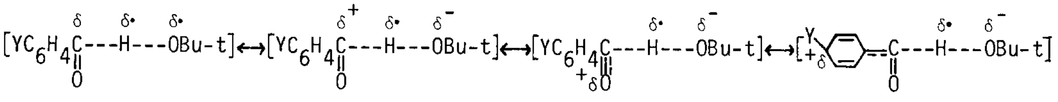
Table 2 Rho Values for the Reactions of Benzaldehydes with t-butoxy Radical

	Hammett Substituent Constant			
	σ^+		σ	
	ρ	r	ρ	r
YC_6H_4CHO + t-BuO	-0 32	0 992	-0 37	0 972

The data of Table 1 were fitted by the method of least squares to the Hammett equation with σ and σ^+ to calculate the rho values in Table 2

Although Walling et al pointed out the complexation of t-butoxy radical with aromatic solvents[19], Sakurai and Hosomi[14] showed that the differential solvent effect as reflected in the change of rho with solvents is rather small not to invalidate our present aim

If BDE effect were the sole factor controlling the reactivities of the benzaldehydes, the transition state should have been of the structure 1, which partially resembles benzoyl radicals

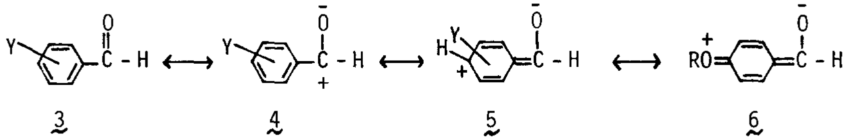


(4)

1 2 2a 2b

In the HTR of toluenes, the major contributing form of the transition states are dipolar rather than neutral, which suggests the charge separation draws more stabilization to the dipolar structure Considering the structures 1 and 2, the former does not have any favoring factors[20] for the stabilization compared to the latter

A characteristic feature of the benzaldehydes is the high degree of polarization of the carbonyl double bond[23], which might influence the reactivities of the aldehydic C-H bonds thereby interfering with the polar effect



(5)

(Y, meta or para-substituents, RO-, p-MeO or p-PhO-)

The polarization was observed to reduce the reactivities towards trichloromethyl radicals significantly when Y were p-MeO and p-PhO groups[16] This could be predictable when we considers the stability of the canonical structure 6 and the like

We may exclude such interference in the present reactions since our result shows good Hammett correlation

It is, therefore, not unreasonable to consider the structure 2 as the major contributing form of the transition state

The Hammett rho value (ρ = -0 32) calculated in the Table 2 may, thus, be interpreted as the measure of the contribution of the dipolar structure 2, i e , the contribution of heterolytic bond cleavage to the transition state of the homolysis

The structure 2 may be additionally stabilized via the charge dispersion to the adjacent oxygen atom to have another resonance structure 2a, which is the Walling's explanation for the higher reactivities of the benzaldehydes than those of toluenes toward t-butoxy radicals[24]

The better correlation with σ^+ than with σ may also point to the dispersion of the positive charge into the phenyl ring to give the structure 2b

In conclusion, polar effect is the solely dominant factor determining the reactivities of the most of the benzaldehydes toward t-butoxy radicals Neither the BDE effect nor the polarization may constitute important elements for the rates of the reactions In short, they are kinetically controlled reactions

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1 Throughout this article, benzaldehydes and toluenes indicate meta and para-substituted ones

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