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COMPARATIVE HAMMETT STUDIES OF IMIDOYL, BENZYLIC, ALDEHYDIC HYDROGENS TRANSFER AND RELATED REACTION BY t-BUTOXYL RADICAL.[1]

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Summary: The polar transition states involved in the hydrogen transfer reactions of N-benzylideneanilines, toluenes, benzaldehydes, and anisoles by t-butoxyl radical in benzene at 130°C have been comparatively discussed in terms of the values of the ρ and the k_a^o/k_d.

The relative rates of hydrogen atom abstractions from organic substrates by t-butoxyl radical have been conveniently measured utilizing the concept of "Free-Radical Clocks".[2] The Hammett correlations thus obtained gave the toluenes ρ= -0.32 at 45°C,[3] the benzaldehydes ρ= -0.32 at 130°C,[4] and the anisoles ρ= -0.41 at 45°C.[5] The former two ρ's exhibited better fit with σ^+ while the ρ of the anisoles with σ, which, nevertheless, could be rationalized likewise by the polar transition states(TS).[6] Although the amount of charge-transfer may be small compared to the S_N1 reaction, the σ^+-correlation may still indicate the delocalization of the positive charge into the phenyl ring, which, in turn, could be prohibited with the anisoles due to the insulation by the oxygen atom of the methoxyl group.[5]

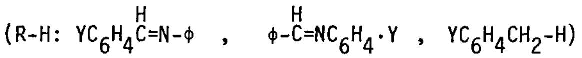
We have undertaken the Hammett studies of imidoyl hydrogen transfer of N-benzylideneanilines[7] and compared the reactivities with those of the related substrates. Recent epr[9,10] and other chemical evidence[8,11] have shown that imidoyl radicals could be the intermediates of hydrogen transfer reaction of imines by t-butoxyl radical.

Reactions at 130°C and for 50 ∿ 60 minutes of degassed and sealed Pyrex ampoules containing variable concentrations(0.05 ∿ 0.2 M) of the substrates(R-H: N-benzylideneanilines[7] and toluenes) with t-butyl peroxide(0.05 M) in benzene led to the formation of t-butyl alcohol and acetone in the subsequent reactions,[12] where the relative rates satisfy eq 3. The rates (k_a/k_d) thus obtained[14] are listed in Table 1, with those of the benzaldehydes.[4]

$$\text{R-H} + \underline{\text{t}}\text{-BuO}\cdot \xrightarrow{k_a} \text{R}\cdot + \underline{\text{t}}\text{-BuOH} \qquad (1)$$

$$\underline{\text{t}}\text{-BuO}\cdot \xrightarrow{k_d} \text{CH}_3\cdot + \text{CH}_3\text{COCH}_3 \qquad (2)$$

$$\frac{[\underline{\text{t}}\text{-BuOH}]}{[\text{CH}_3\text{COCH}_3]} = \frac{k_a}{k_d}[\text{R-H}] \qquad (3)$$



$$(\text{R-H: } \text{YC}_6\text{H}_4\overset{\text{H}}{\text{C}}\text{=N-}\phi \ , \quad \phi\text{-}\overset{\text{H}}{\text{C}}\text{=NC}_6\text{H}_4\cdot\text{Y} \ , \quad \text{YC}_6\text{H}_4\text{CH}_2\text{-H})$$

Table 1. Relative Reactivities of Imidoyl, Benzylic and Aldehydic Hydrogens toward t-Butoxyl Radical at 130°C in Benzene.

Substituents (Y)	$(k_a/k_d)^{a,b}$			
	$YC_6H_4\overset{H}{C}=N\text{-}\phi$ 1a	$\phi\text{-}\overset{H}{C}=NC_6H_4\cdot Y$ 1b	$YC_6H_4CH_2\text{-}H$	$YC_6H_4C(O)\text{-}H^c$
$p\text{-}OCH_3{}^d$	0.47^e	--	0.388/3	--
$p\text{-}CH_3{}^d$	2.01	1.22	0.239/3	17.4
$m\text{-}CH_3{}^d$	1.01	0.83	--	13.5
p-F	0.54^e	0.48^e	0.189/3	--
H	0.82	0.82	0.193/3	13.3
p-Cl	0.65	0.60	0.176/3	11.8
p-Br	0.62	0.54	0.157/3	11.6
m-Cl	--	0.39	0.118/3	9.7
m-CN	0.27	--	--	8.8

(a) Product analyses were performed with 8 ft. x 1/8 in. stainless steel column packed with 10% diisodecyl phthalate on Chromosorb W using Varian 4600 Vista equipped with FID and CDS 401 data system. (b) Error limits are within ±3%, being average deviations of three or more experiments. (c) Taken from reference 4. (d) Corrections were made for the hydrogen abstractions from either the methoxyl or methyl group. (e) The remarkable reduction of the reactivities could be caused via the polarization of the C=N bond by the para-substituents, which makes the imidoyl hydrogen assuming some vinylic character. Similar polarization had been observed to reduce the reactivities of the benzaldehydes toward trichloromethyl radical. Refer to Lee, K. H. Tetrahedron, 1968, 24, 4793.

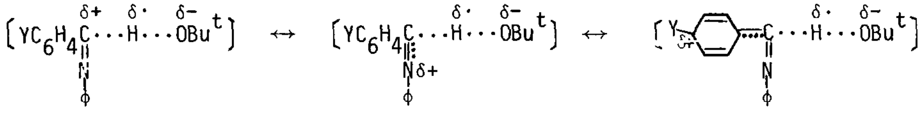
Table 2. Hammett ρ Values, their Correlation Factors and Relative Reactivities of per C-H Bond of N-Benzylideneaniline, Toluene, Benzaldehyde and Anisole toward t-Butoxyl Radical at 130°C in Benzene.

R-H + t-BuO·	Hammett Substituent Constant^a				(k_a^o/k_d)
	σ^+		σ		
R-H	ρ	r	ρ	r	
$YC_6H_4\overset{H}{C}=N\text{-}\phi$, 1a	-0.98	0.993	-1.04	0.961	0.82
$\phi\text{-}\overset{H}{C}=NC_6H_4\cdot Y$, 1b	-0.72	0.990	-0.81	0.977	0.82
$YC_6H_4CH_2\text{-}H$,	-0.42	0.992	-0.66	0.942	0.064
$YC_6H_4C(O)\text{-}H^b$,	-0.32	0.992	-0.37	0.972	13.3
$YC_6H_4OCH_2\text{-}H$,	--	--	--	--	0.046^c

(a) Ritchie, C. D.; Sager, W. F. Progr. Phys. Org. Chem. 1964, 2, 334.
(b) Taken from reference 4.
(c) For the anisoles, only k_a^o/k_d has been calculated by the same method.[14]

The data in Table 1 were fitted by the method of least square to give the ρ's, showing better fit with σ^+ as shown in Table 2, which contains also the relative reactivities (k^o_a/k_d) of per C-H of the unsubstituted substrates, i.e. $C_6H_5\overset{H}{C}=NC_6H_5$, $C_6H_5CH_2$-H, $C_6H_5C(O)$-H, $C_6H_5OCH_2$-H.

The better correlation with σ^+ could indicate S_N1-like polar TS,[15] which would retain more degrees of freedom than that of S_N1 reaction because of the longer separation of the ion-pair probably with less amount of charge-transfer.[16] The TS structure of the N-benzylideneanilines could be similar to that of the benzaldehydes.[4]



2 3 4

The ρ(= -0.98) for <u>1a</u> is more negative than the ρ(= -0.72) for <u>1b</u>, which could be interpreted as that the TS is more contributed by the structure <u>2</u> than by <u>3</u>. Since both ρ's of <u>1a</u> and <u>1b</u> are much more negative than the ρ(= -0.32) of the benzaldehydes, the former TS's could be more polar and involve, accordingly, more C···H bond cleavage than the latter.[15] Greater bond breaking should require larger enthalpy of activation[16] leading to the correspondingly less reactivity, which may be reflected in the values of k^o_a/k_d, i.e. 0.82 and 13.3 for the two reactions, respectively. Since the ρ(= -0.42) of the toluenes is intermediate between those of the N-benzylideneanilines (ρ= -0.98, -0.72) and the benzaldehydes (ρ= -0.32), the TS of toluene may involve the corresponding polarity and the C···H breaking, which might give toluene $0.82 < k^o_a/k_d < 13.3$. Nonetheless, toluene shows $k^o_a/k_d = 0.064$ exhibiting exceedingly low reactivity compared to N-benzylideneaniline and benzaldehyde. The TS of toluene could not involve a canonical form equivalent to <u>3</u>, which, more or less, prevents delocalization of the positive charge. This inhibition of the delocalization could *a)* destabilize the cationic moiety and *b)* increase the attraction of the ion-pair forming a tighter TS.[16] The factor *a* could increase the enthalpy of activation required for the bond breaking and the *b* reduce entropy of activation, both of which thus serve effectively to reduce the reactivity.[17] The delocalization would be even worse with anisole than with toluene. The oxygen atom of the methoxyl group may prevent[5] the dispersion of the charge giving rise to the least reactivity of $k^o_a/k_d = 0.046$.

In conclusion, the reactivity could be controlled by 1) the degree of C···H breaking and 2) the delocalizability of the resulting cation. The reactivities, therefore, decrease as follows, benzaldehyde[18] >> N-benzylideneaniline > toluene ≈ anisole.

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18. Recently, absolute rate constants for hydrogen abstraction from the benzaldehydes by *t*-butoxyl radical at 130°C have been reported to be in a range close to the diffusion-controlled limit (*ca.* $10^8\ M^{-1}S^{-1}$). Refer to Chatgilialoglu, C.; Lunazzi, L.; Macciantelli, D.; Placucci, G. J. Am. Chem. Soc. 1984, 106, 5252.

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