BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 41 1928—1937 (1968)

Hydrogen Abstraction Reaction of α-Heteroatom Substituted Compounds by *t*-Butoxy Radical*[1]

Kenji UNEYAMA, Hiroshi NAMBA and Shigeru OAE

Department of Applied Chemistry, Faculty of Engineering, Osaka City University,
Sugimoto-cho, Sumiyoshi-ku, Osaka

(Received February 19, 1968)

Hydrogen abstraction reactions of various α-substituted compounds were examined in chlorobenzene using di-*t*-butyl peroxide. The reactivities are not satisfactorily correlated with σ^* values of the substituents. The relative rates of substituted anisoles, *N,N*-dimethylanilines and phenyl methyl sulfones give good correlations with Hammett σ values with ρ values of -0.39, -0.42 and -0.2 respectively, but those of thioanisoles requires an additional term due to conjugative effect as described in $\log k/k_0 = -0.11(\sigma + 0.75\Delta\sigma_{R^+})$ in order to get a good Hammett correlation. These results were discussed in terms of a combination of an inductive effect, an electron-releasing and an electron-sharing conjugation.

In connection with our recent work on the 3d orbital resonance in divalent sulfides, we have extended our investigation to the hydrogen abstraction reaction of various sulfur compounds and related α-heteroatom substituted compounds by *t*-butoxyl radical. In the carbanion forming reaction such as the base catalyzed hydrogen-deuterium exchange reaction of various mercaptoles,[1] the base catalyzed decarboxylation reactions of various α-alkyl- and arylmercaptoacetic acids,[2] the E_2 reaction of β-chloroethyl phenyl sulfides[3] and also the acid dissociation equilibria of phenols

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*[1] Paper XI on 3d-orbital Resonance in Divalent Sulfides.

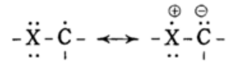
[1] S. Oae, W. Tagaki and A. Ohno, *Tetrahedron*, **20**, 417, 427 (1964).

[2] a) S. Oae, W. Tagaki, K. Uneyama and I. Minamida, *ibid.*, in press. b) W. Tagaki, K. Uneyama, I. Minamida, Kim Yon Hey, Y. Ikeda and S. Oae, This Bulletin, **39**, 917 (1966).

[3] Y. Yano and S. Oae, *Tetrahedron*, in press.

which bear either mercapto or other related sulfur substituents in the benzene rings,[4] all the mercapto groups showed rate enhancing effect, while the corresponding oxygen counterparts showed rate retardation and these results are explained on the basis of the stabilization of carbanion incipiently formed in the transition state by the 3d orbital resonance effect of divalent sulfur atom as shown in Eq. (1).[5] Meanwhile in the carbonium ion forming reaction such as the solvolyses of α-substituted methyl chlorides, alkoxyl group is known to give greater rate enhancement than mercapto group[6] due to the more effective electron-releasing conjugative effect of alkoxy group than that of the sulfur counterpart. The effects of divalent sulfur and alkoxy group in the radical forming reaction have not been investigated quantitatively and hence are quite interesting subjects for investigation in connection with these conjugative effects, namely electron-releasing conjugation[7] like (2) and electron-sharing conjugation like (3), since the electric environment of the radical reaction is vastly different from these of the ionic reactions and other factor may become important.

$$-\mathrm{S}-\underset{|}{\overset{\ominus}{\mathrm{C}}}- \longleftrightarrow -\overset{\ominus}{\dot{\mathrm{S}}}=\underset{|}{\mathrm{C}}- \qquad (1)$$



$$-\underset{\cdot\cdot}{\ddot{\mathrm{X}}}-\underset{|}{\dot{\mathrm{C}}}- \longleftrightarrow -\overset{\oplus}{\underset{\cdot\cdot}{\dot{\mathrm{X}}}}-\overset{\ominus}{\underset{|}{\ddot{\mathrm{C}}}}- \qquad (2)$$

$$-\underset{\cdot\cdot}{\ddot{\mathrm{X}}}-\underset{|}{\dot{\mathrm{C}}}- \longleftrightarrow -\underset{\cdot\cdot}{\dot{\mathrm{X}}}=\underset{|}{\mathrm{C}}- \qquad (3)$$

Russell *et al.* investigated the hydrogen abstraction from α-methyl or methylene group attached to heteroatoms by phenyl radical and found that alkoxyl, mercapto and amino groups have substantial rate enhancing effects as compared with phenyl group and explained these rate-enhancements in terms of the stabilization of the incipient radicals by electron-releasing conjugative effect of α-substituents as shown in Eq. (2). Meanwhile, the electron-sharing conjugation[8,9] like (3) has been proposed on the basis of the remarkably large Q values of alkyl vinyl sulfides and vinylidene mercaptals as compared with those of the oxygen analogs, methyl vinyl sulfone and trimethylvinylsilane in the copolymerization with styrene. The stabilization of the radicals, namely the large Q values, has been proposed to be due to the delocalization of an odd electron into the hybridized orbital between 2p-orbital on α-carbon atom and 3d-orbital on sulfur atoms, and this type of conjugative effect can display only with those groups of the 2nd row elements bearing at least one lone electron pair and not with these without any lone-pair or with those of the lst row elements. The electron-sharing conjugation also can satisfactorily explain the orientation of the thiyl radical to mercapto- and alkoxyacetylenes.[10] However, the hypothesis of the electron-sharing conjugation effect has to be tested with more critical and quantitative experiments. With these background thoughts, we have studied the hydrogen abstraction reaction of various α-substituted compounds by *t*-butoxy radical and this paper will discribe the detailed account of the results and discussion especially as to what extent, electron-releasing or/and electron-sharing conjugative effects would control the reactivities and also change the mechanism of the reaction.

Results and Discussion

Kinetics. The decomposition of di-*t*-butyl peroxide was carried out in chlorobenzene at 130℃ ± 0.5℃, for 42 hr during which the peroxide was completely decomposed.[11] The *t*-butoxy radical formed by the thermal decomposition of the peroxide is mainly consumed through the following two processes. The one is the β-scission of *t*-butoxy radical into acetone and methyl radical as shown by Eq. (4) and the other is the hydrogen abstraction from a hydrogen donor compound (RH) giving *t*-butanol Eq. (5). In these experiments, the total yields of acetone and *t*-butanol combined were always more than 95% with all the substrates examined; therefore, the hydrogen abstraction and the β-scission consist of the main portion of the reaction. Thus, the relative reactivity of reactions (4) to (5) is given by Eq. (6),[12]

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[4] S. Oae, M. Yoshihara and W. Tagaki, This Bulletin, **40**, 951 (1967)

[5] C.C. Price and S. Oae, "Sulfur Bonding," Ronald Press Co., N.Y. (1962).

[6] H. Böhme, H. Fischer and R. Frank, *Ann.*, **563**, 54 (1949)

[7] R.F. Bridger and G.A. Russell, *J. Am. Chem. Soc.*, **85**, 3754 (1963)

[8] C.C. Price and J. Zomlefer, *ibid*, **72**, 14 (1950); C.C. Price and T.C. Schman, *J. Polymer Sci.*, **16**, 577 (1955); C.E. Scott and C.C. Price, *J. Am. Chem. Soc.*, **81**, 2670, 2672 (1959). See also Ref. 5, p. 26.

[9] W. Tagaki, S. Kiso, T. Tada, R. Nomura and S. Oae, This Bulletin, submitted.

[10] H.C. Volger and J.F. Arens, *Rec. Trav. Chim.*, **77**, 1170 (1958); J. Bonnema and J. F. Arens, *ibid*, **79**, 1137 (1960); H.J. Alkema and J.F. Arens, *ibid*, **79**, 1257 (1960).

[11] J.H. Raley, F.F. Rust and W.E. Vaughan, *J. Am. Chem. Soc.*, **70**, 1336 (1948)

[12] J.H. Raley, F.F. Rust and W. E. Vaughan, *J. Am. Chem. Soc.*, **70**, 1336 (1948).

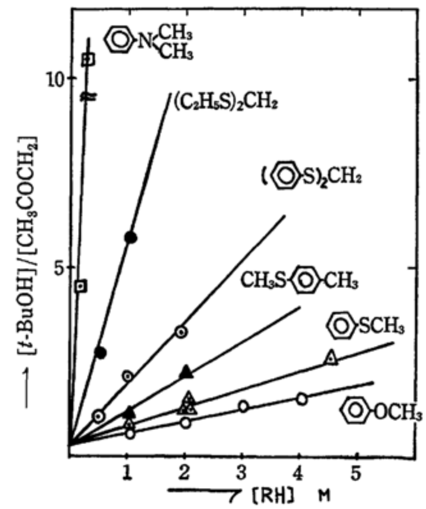


Fig. 1. Plot of [t-BuOH]/[CH$_3$COCH$_3$] against [RH].

$$t\text{-BuO}\cdot \xrightarrow{k_d} CH_3COCH_3 + CH_3\cdot \quad (4)$$

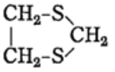
$$t\text{-BuO}\cdot + RH \xrightarrow{k_a} t\text{-BuOH} + R\cdot \quad (5)$$

$$t\text{-BuOH}/CH_3COCH_3 = k_a/k_d \times [RH] \quad (6)$$

where k_d and k_a are the rate constants of the decomposition and the hydrogen abstraction respectively, while [RH] is the concentration of a substrate. Applicability of this Eq. (6) to all the substrates can be tested by plotting their t-BuOH/CH$_3$COCH$_3$ values againt [RH] and we got a straight line, from whose slope k_a/k_d was able to be calculated. Applications for a few substrates are illustrated in Fig. 1.

Influence of α-Substituent. The relative reactivities k_a/k_d of all the substrates and those of hydrogen abstraction relative to toluene are summarized along with the σ^* values of all the substituents in Table 1. Inspection of the data reveals a few interesting points worthy to be noted in the following paragraphs. 1) Anisole, thioanisole and N,N-dimethylaniline react much faster than

TABLE 1. RELATIVE REACTIVITIES OF α-HYDROGEN ATOM[a)]

Compound	k_a/k_d $\times 10^{d)}$	Rel. reactivity[c)]	$\sigma^{*d)}$
-CH$_3$	0.944	1.00	0.215
-OCH$_3$	1.36	1.44	0.95[e)]
-SCH$_3$	2.00	2.12	0.77
$-N\begin{smallmatrix}CH_3{}^{9)}\\CH_3\end{smallmatrix}$	77.3	81.9	
-SO$_2$CH$_3$	0.05	0.05	1.32[f)]
$(CH_3C_2)_2S$[h)]	6.70	7.10	0.46
$(C_2H_5S)_2CH_2$[i)]	15.4	16.3	1.12
	46.4	49.2	1.02
(-S)$_2$CH$_2$	9.44	10.0	1.54
(-S)$_3$CH	13.1	13.9	2.31
(-O)$_2$CH$_2$	3.91	4.14	1.90

a) In chlorobenzene at 130°C. Most of substrates were examined in 0.5—2.0 M concentration and di-t-butyl peroxide was 0.107 M.

b) Reactivity per one hydrogen.

c) Relative reactivity to toluene.

d) See Ref. 2c), and R. W. Taft. Jr., "Steric Effects in Org. Chem.," ed. by M.S. Newman, John Wiley & Sons, Inc., New York (1956).

e) Reported value is 0.85 by R.W.Taft, Jr., See Ref. d.

f) σ^* value of CH$_3$SO$_2$CH$_2$- group.

g) 0.1—0.3M of substrate and 0.043 M of (t-BuO)$_2$.

h) Methylene was assumed to be a reactive hydrogen source.

i) Reactivity of hydrogen (H_α) surrounded by two geminal sulfur atom was calculated as follows.

$$(k_a/k_d)H_\alpha = 1/2\{\text{Total reactivity of } (C_2H_5S)_2CH_2 \text{—Total reactivity of } (C_2H_5)_2S\}$$

TABLE 2. RELATION OF REACTIVITY WITH THE NUMBER OF α-SUBSTITUENT[a)]

X_nCH_{4-n}	X	-S	-O	-[b)]	-[c)]	CH$_3$[d)]	CH$_3$[e)]
Primary	n=1	1	1	1	1	1	1
Secondary	2	4.7	2.9	4.7	4.2	3.2	8
Tertiary	3	6.6	—	9.6		5.1—6.4	44

a) Reactivity of α-hydrogen atom toward t-BuO· as the number of substituents was changed.

b) By t-BuOCl at 40°C, C. Walling and B.B. Jacknow, *J. Am. Chem. Soc.*, **82**, 6108 (1960).

c) By (t-BuO)$_2$ at 135°C. A.L. Willams, E.A. Oberright and J.B. Brooks, *ibid.*, **78**, 1190 (1956).

d) By (t-BuO)$_2$ at 135°C, toluene, ethylbenzene, and cumene are substrates.

e) Hexamethylethane, neopentane, and n-butane are substrates by t-BuOCl at 40 °C. C. Walling and W. Thaler, *ibid.*, **83**, 3877 (1961).

toluene, while *N,N*-dimethylaniline is the fastest reacting substrate among all of the substrates examined and thioanisole has a slightly larger rate than anisole, whereas very little hydrogen abstraction takes place with phenyl methyl sulfone. This markedly slow rate of phenyl methyl sulfone is quite contrary to the case of the carbanion forming reaction as seen in the decarboxylation reaction,[2] in which phenylsulfonyl group accelerates the reaction more than phenylmercapto group. 2) The ring compound (ethanedithioformal) reacts faster than the corresponding acyclic compound (diethylmercaptoformal). 3) Successive substitution of either phenylmercapto or phenoxyl group at α-carbon atom of either thioanisole or anisole respectively leads to a gradual rate increment (see Table 2). 4) No reasonable correlation between reactivities of substrates (XCH_3) and σ^* values of substituents (X) is found and only scattered points are obtained when one plots log k_a/k_d against σ^* values as shown in Fig. 2. These observations reveal that the reactivities of α-hydrogen are not determined simply by inductive effect of α-substituents and that those substituents that have heteroatoms bearing at least one lone electron pair at α-position enhance the rate of hydrogen absotraction. The successive substitution of phenylmercapto and phenoxyl groups at α-position appears to increase the relative rate considerably. Thus diphenylmercaptoformal is 5 times as reactive as thioanisole, while tris (phenylmercapto) methane has rate 7 times larger than that of thioanisole. This gradual rate enhancement with additional substitution of same substituent on α-carbon atom can be seen with all the substituents, however, the amount of the rate enhancement by one additional substituent seems to be nearly identical independently of the nature of substituent in spite of the different induc-

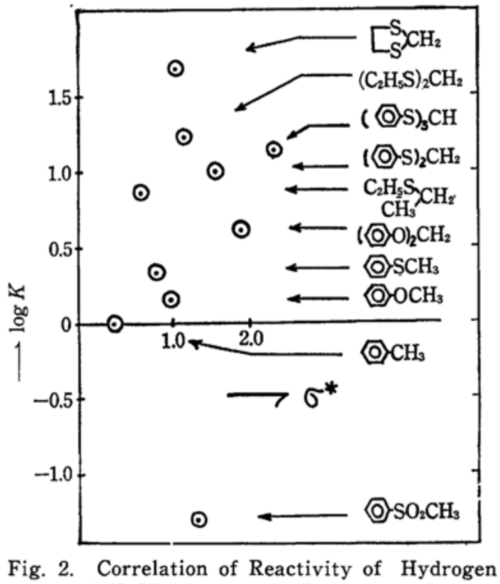


Fig. 2. Correlation of Reactivity of Hydrogen of X_nCH_{4-n} toward *t*-BuO· radical with σ^* of Substituent.

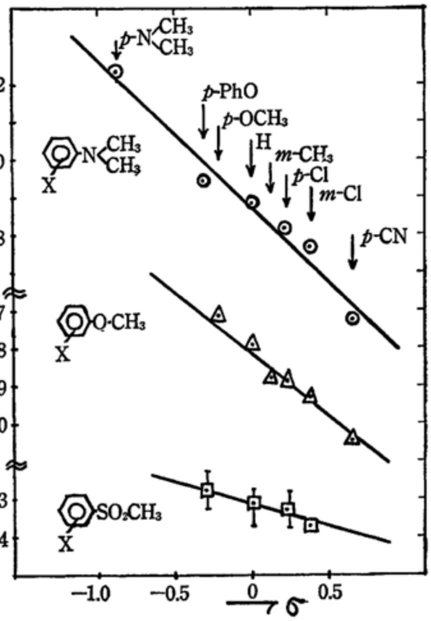


Fig. 3. Hammett correlation of anisole, *N,N*-dimethylaniline and methyl phenyl sulfone.

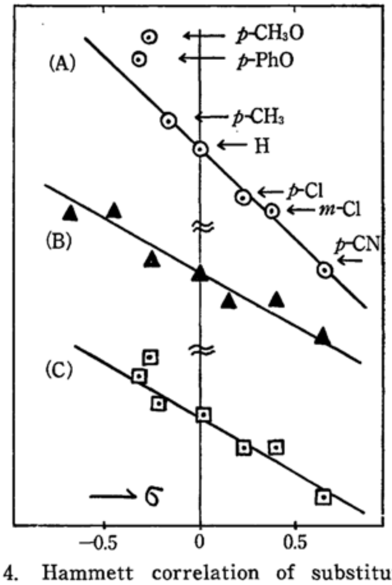


Fig. 4. Hammett correlation of substituted thioanisoles.

(A) $\log k/k_0 = -0.12\ \sigma$

(B) $\log k/k_0 = -0.11\ (\sigma + 0.75\ \Delta\sigma_{R+})$

(C) $\log k/k_0 = -0.11\ \sigma + 0.1 \cdot E_R$

TABLE 3. RING SUBSTITUENT EFFECTS OF ANISOLE, THIOANISOLE N,N-DIMETHYLANILINE AND METHYL PHENYL SULFONE[a]

$k_a/k_d\times 10$ Substituent	 -OCH$_3$[b]	 -SCH$_3$[b]	 -SO$_2$CH$_3$[c]	 -N$\begin{matrix}\text{CH}_3\\\text{CH}_3\end{matrix}$[d]
p-N$\begin{matrix}\text{CH}_3\\\text{CH}_3\end{matrix}$	—	—	—	172
p-PhO	—	2.33	0.053	88.4
p-CH$_3$	1.74	2.40[e]	—	—
p-CH$_3$	—	2.10[f]	—	—
H	1.36	2.00	0.048	77.4
p-Cl	1.12	1.87	0.047	65.2
m-Cl	1.00	1.83	0.040	58.1
p-CN	0.78	1.67	—	36.6
m-CH$_3$O	1.13	—	—	—

a) All the values of k_a/k_d are the averages of more than two runs.

b) 2.00 M in chlorobenzene with 0.107 M of di-t-butyl peroxide.

c) 1.00 M.

d) 0.1 M solution with 0.043 M of $(t\text{-BuO})_2$.

e) The reactivity of hydrogen of methoxyl group was subtracted from the total reactivity (3.76) as follows. Substituted anisole gave a satisfactory Hammett σ correlation and σ value of para-methylmercapto group is 0.00, therefore, the reactivity of hydrogen of methylmercapto group in para methoxythioanisole is 3.76−1.36 (reactivity of anisole) = 2.40.

f) Substituted toluene is known to give σ^+ correlation (see Ref. 22) and ρ is −0.38 (σ^+) at 125 °C with di-t-butyl peroxide.
The reactivity of para-methyl group is

$$\log k = -0.38(-0.604) + \log 0.944 = 0.205,\ k = 1.60.$$

Therefore, the reactivity of hydrogen of methylmercapto group is

$$3.70(\text{total reactivity}) - 1.60 = 2.10.$$

TABLE 4. HAMMETT ρ VALUE OF HYDROGEN ABSTRACTION REACTION BY t-BUTOXYL RADICAL

Substrate	Solvent	Temp. (°C)	ρ	r[d]
 -CH$_3$	Chlorobenzene	125	−0.55	
		135	−0.38(σ^+)[a]	
		45	−0.32(σ^+)[b]	0.973
	Freon-113	45	−0.35(σ^+)[b]	0.989
 -OCH$_3$	Chlorobenzene	130	−0.39	0.986
		45	−0.41[c]	
 -SCH$_3$	Chlorobenzene	130	−0.15	0.956
			−0.11(σ^+)	0.970
			−0.11($\sigma+0.75\,\Delta\sigma_R{}^+$)	0.986
 -N$\begin{matrix}\text{CH}_3\\\text{CH}_3\end{matrix}$	Chlorobenzene	130	−0.42	0.981
 -SO$_2$CH$_3$	Chlorobenzene	130	−0.2	—

a) T. Yamamoto, M. Hasegawa and T. Nakamura, see Ref. 22.

b) H. Sakurai and A. Hosomi, *J. Am. Chem. Soc.*, **89**, 458 (1967).

c) H. Sakurai and A. Hosomi, *Conference on Org. Reaction Mechanism, Kyoto* (1067). Di-t-butyl peroxalate was used.

d) Correlation coefficient.

tive effects of these substituents, if one carefully examines the data in Table 2, which includes other reported data on methyl[13] and phenyl[14] groups. This fact suggests that all the substituents including methyl, phenyl, phenoxyl and phenylmercapto groups when they are substituted additionally at α-position give some additional stabilization to the incipiently developing radicals by the conjugative effect of the respective groups.

Hamett Relationship. The relative reactivities found for these substituted anisole, thioanisole, *N,N*-dimethylaniline, and phenyl methyl sulfone derivatives are treated with the Hammett equation. The results are shown in Figs. 3 and 4, and Tables 3 and 4, while the Hammett ρ values of these reactions are listed in Table 4. Table 4 shows that the logarithms of the relative rates of the substituted anisoles and *N,N*-dimethylanilines can be satisfactorily correlated with normal Hammett σ values with ρ values of -0.39 and -0.42 respectively and the sulfones also give σ correlation with $\rho=-0.2$ although reproducibility of k_a/k_d values is by no means excellent for the sulfonyl compounds. The substituted thioanisoles show somewhat different pattern of substituent effect. While *p*-CN, *p*-Cl, *m*-Cl, H and *p*-CH_3 groups are well correlated with σ values, *p*-CH_3O and *p*-PhO groups give slight deviations from the linearity of correlation line with the value of $\rho=-0.15$ and the correlation coefficient of 0.956. Yukawa-Tsuno's treatment[15] gave the best line with $r=0.75$, to give an equation $\log k/k_0=-0.11(\sigma+0.75\,\Delta\sigma_R^+)$ with correlation coefficient of 0.986, while Brown-Okamoto's σ^+[16] correlation gave $\rho=-0.11$, correlation coefficient of 0.970. Yamamoto's treatment[17] of E_R value also gave a relatively good correlation with $\rho=-0.12$, and the correlation coefficient of 0.980, but methoxyl group falls off substantiallyl.

We used Yukawa-Tsuno'st reatment because of the following reasons. 1) calculated γ value, which is a rough measure of resonance contribution[17] is very small, namely, 0.1, in this free radical reaction of hydrogen abstraction of thioanisole when one compares the value with those observed in many other examples.[18] 2) The carbon atom of the reacting center is considered to bear a partial positive charge in the transition state because the hydrogen abstracting agent in this reacton is *t*-butoxyl radical. 3) The trend of the α-substituent effects in this hydrogen abstraction reaction is similar to that found in the solvolyses of α-substituted methyl chlorides, but not to that in the carbanion-forming reactions as seen in Table 5. 4) The kinetic isotope effect of the reaction measured with both α-deuterated and undeuterated thioanisoles, *i.e.* 3.2 at 130℃, which is considered to be a relatively large as compared to the others[19] listed in Table 6, indicates that C–H bond of thioanisole

TABLE 5. COMPARISON OF THE EFFECT OF SULFUR SUBSTITUENTS TO CARBANION, RADICAL AND CARBONIUM IONS ON α-CARBON ATOM

Substituent	$-\mathrm{X}-\overset{\ominus}{\underset{\vert}{\mathrm{C}}}-$[a]	$-\mathrm{X}-\overset{\cdot}{\underset{\vert}{\mathrm{C}}}-$[b]	$-\mathrm{X}-\overset{\oplus}{\underset{\vert}{\mathrm{C}}}-$[c]
C_2H_5S-	1.0	1.0	1.0
 -S-	10^3	0.6	0.005
 -SO_2-	$>10^5$	0.02	no reaction

a) Base catalyzed decarboxylations of α-substituted carboxylic acids. S. Oae, W. Tagaki, K. Uneyama and I. Minamida, *Tetrahedron*, in press.

b) Hydrogen abstraction by *t*-butoxyl radical in this work.

c) Solvolysis reaction of α-substituted methyl chlorides (X-CH_2Cl). H. Böhme, H. Fischer and R. Frank, *Ann.*, **563**, 54 (1949).

TABLE 6. KINETIC ISOTOPE EFFECT.

Substrate	k_H/k_D	Solvent	Radical	Temp. ℃
 -SCH_3[a]	3.2	PhCl	*t*-BuO·	130
 -CH_2CH_3[b]	3.7	PhCl	*t*-BuO·	120
 -CH_3[c]	2.4	Freon-113	*t*-BuO·	45

a) Hydrogen of methyl group was 33% of deuterium content.
$k_H=0.200$, $k_{obs}=0.153$, hence, k_D calcd$=0.062$, see experimental.

b) G. A. Russell, *J. Am. Chem. Soc.*, **79**, 3871 (1957).

c) H. Sakurai, *Symposium on Hammett Relationship, Kyoto*, (1967).

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13) C.Walling and W.Thaler, *J. Am. Chem. Soc.*, **85**, 3754 (1963).

15) C. Walling and B.B. Jacknow, *ibid*, **82**, 6108 (1960); J. H. Brooks, *Trans. Faraday Soc.*, **53**, 327 (1957).

15) Y. Yukawa and Y.Tsuno, This Bulletin, **32**, 960, 965, 971 (1959).

16) H.C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **79**, 1913 (1957); Y. Okamoto and H.C. Brown, *J. Org. Chem.*, **22**, 485 (1957).

17) T.Azumi and T.Yamamoto, *Reports of Himeji Institute of Techn.*, **11**, 152 (1960); T. Otsu and T. Yamamoto, *Yuki Gosei Kagaku Kyokaishi* (*J. Soc. Org. Synth. Chem. Japan*), **23**, 643 (1965).

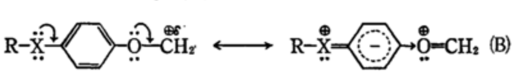
18) See T. Yamamoto, his Ph. D. works in Osaka City Univ. (1966), in which various Hammett relation of radical reactions are summarized.

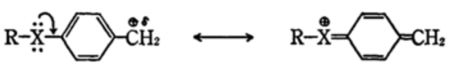
19) G. A. Russell, **79**, 3871 *J. Am. Chem. Soc.*, (1957).

is broken at the transition state sufficiently enough to receive a noticeable assistance of the conjugative effect of the ring substituents *via* the divalent sulfur atom.

Therefore, electron-releasing conjugative effect of substituent must be responsible. Alkoxyl, mercapto and amino groups are known to be markedly electron-releasing in the electron-donating reactions, and the order of the effect is the following, $R_2N- \gg R-O- > R-S- > Ph- \gg PhSO_2-$.*2 This order of elecron-releasing effect can explain the sequence of the relative reactivities of the heteroatom-substituted compounds. This is quite understandable in view of the fact that *t*-butoxyl radical is highly electronegative and the transition state of this hydrogen abstraction reaction would be of somewhat polar nature as was postulated previously by Russell in the similar hydrogen abstraction reaction with phenyl radical. The slightly larger reactivity of thioanisole as compared with anisole may be due to the stronger inductive effect of phenoxyl group than that of phenylmercapto group and/or a possible electron-releasing effect from aryl group additionally transmitted to the reaction center through the divalent sulfur atom. Russell *et al.* also reported that thioanisole is three times as reactive as anisole in hydrogen abstraction by phenyl radical. Taking into account the less electronegativity of phenyl radical and the larger kinetic isotope effect (k_H/k_D), (which means the greater bond breaking in the transition state) than that with *t*-butoxy radical, this rather large rate difference is considered to be due to the greater stabilization of thiophenylmethyl radical ($PhSCH_2\cdot$) by the electron-sharing conjugation. Such an effect which we call electron-sharing conjugation is not conceivable in the case of anisole because of the lack of available 3d-orbitals. Though the effect is small, this conjugative effect by divalent sulfur atom is playing a definite role in the reaction of thioanisole derivatives as will be discussed.

In the previous paragraph it was shown that both anisole*3 and *N,N*-dimethylaniline give good correlations with Hammett σ constants. This successful σ-correlation for both substituted anisoles and *N,N*-dimethylanilines indicates that electron-releasing π-inductive effects of these *p*-substituents like *p*-methoxyl and *p*-phenoxyl groups are transmitted inductively to the terminal carbon atom through the chain as illustrated by (B).


(B)


(C)


(D)

Meanwhile, thioanisole derivatives apparently display an additional conjugative effect of substituents and its Hammett relationship is described in Eq. (7),

$$\log k/k_0 = -0.11\ (\sigma + 0.75\Delta\sigma_R{}^+) \qquad (7)$$

although the degree of the additional conjugative effect is somewhat smaller ($r=0.75$) than benzyl radical ($r=1.0$), in which σ^+ plot is known to give a satisfactory correlation.[22] The successful σ^+ correlation suggests that a direct conjugative interaction between the reacting carbon center and the substituents is operative and such a conjugation is possible only through the 3d-orbital resonance of divalent sulfur atom shown by (D). Sulfonyl group, having no electron pair available for such a conjugation retards the rate of hydrogen abstraction by *t*-butoxyl radical and σ correlation gives a better fit than σ^+ correlation for the rates of substituted sulfonyl compounds.

As a final remark, we may conclude that the rate enhancement by α-heteroatoms in this reaction is mainly due to the electron-releasing conjugative effect and both substituted anisoles and *N,N*-dimethylanilines give good Hammett σ correlations, while in the

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*2 $(\sigma_p{}^+ - \sigma_m{}^+)$ values of $(CH_3)_2N$, CH_3O, CH_3S, C_6H_5, and CH_3SO_2- are -1.49, -0.83, (-0.75 for Ph-O), -0.76, -0.29 and 0.12 respectively from H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80**, 4979 (1958) ; H.H. Jaffe, *Chem. Revs.*, **53**, 222 (1953). $\sigma_m{}^+$s of phenyl, *N,N*-dimethyl and phenoxy are not available, hence σ_m values were used for $\sigma_m{}^+$. σ^+ of sulfonyl group is not available, therefore $(\sigma_p - \sigma_m)$ was used instead of $\sigma_p{}^+ - \sigma_m{}^+$. This treatment is reasonable when one recalls the similarity of $\sigma_p{}^+$ values with σ_p values of electron-withdrawing group.

*3 Sakurai and Hosomi reported also $\rho = -0.41$ in the hydrogen abstraction of substituted anisoles by *t*-butoxyl radical at 45°C[20] and the thermal decomposition of ring substituted *t*-butyl perphenoxyacetate in ethylbenzene is known to give σ correlation with ρ value of -1.18.[21]

20) H.Sakurai an A.Hosomi, *Conference on Org. Reaction Mechanism, Kyoto, Japan* (1967).

21) C. Ruchardt, H. Bock and I. Ruthardt, *Ang. Chem.*, **78**, 268 (1966).

22) H.Sakurai and A.Hosomi, *J. Am. Chem. Soc.*, **89**, 458 (1967); T. Yamamoto, M. Hasegawa and T. Nakamura, *Anual Meeting of the Chem. Soc., Japan, Chugoku-Shikoku Area Meeting* (1965).

case of substituted thioanisoles, an additional conjugative effect of substituents such as *p*-methoxyl and *p*-phenoxyl group, appears to be transmitted *via* sulfur atom perhaps using 3d-orbitals of divalent sulfur atom and the rates are correlated better with σ^+ values. More clear evidence of electron-sharing conjugation of divalent sulfur atom may be obtained in the hydrogen abstraction reaction with more neutral phenyl radical and the work on this line is in progress in these laboratories.

Experimental

Preparations of Materials. *Substituted Anisoles.* *p*-Chloro-, *m*-chloro-, *p*-methoxy- and *m*-methoxyanisoles were synthesized by methylation of the corresponding phenols with dimethyl sulfate in alkaline methanol solution. *p*-Cyanoanisole was prepared by Sandmeyer reaction of diazonium salt of *p*-anisidine.

Substituted Thioanisoles. The methylation of thiophenol, *p*-chloro- and *p*-methylthiopheno land *p*-methylmercaptophenol by dimethyl sulfate gave the corresponding thioanisole derivatives in good yields. *p*-Methylmercaptobenzonitrile was prepared from Sandmeyer reaction of *p*-methylmercaptoaniline in 23% yield and recrystallized from methanol as colorless crystals melting at 63—64°C. *p*-Methylmercaptoaniline was obtained by the usual methylation of *p*-aminothiophenol, which was prepared by the treatment of *p*-chloronitrobenzene with sodium sulfide nonanhydrate as described by Gilman.[23] *m*-Chlorothioanisole was prepared by allowing to react sodium methylmercaptide with diazonium salt of *m*-chloroaniline in an aqueous alkaline solution.[24] *p*-Methylmercaptophenyl phenyl ether was prepared by heating the mixture of *p*-methylmercaptophenol[25] and bromobenzene in a concentrated aqueous potassium hydroxide solution in the presence of a small amount of copper powder at 150°C as described by Brewster.[26]

Preparation of Substituted N,N-Dimethylaniline Derivatives. *p*-Dimethylaminobenzonitrile was prepared by Sandmeyer reaction of *p*-amino-*N,N*-dimethylaniline and purified by recrystallization from methanol as colorless crystals melting at 73—74°C. 4-*N,N*-dimethylaminodiphenyl ether was prepared by methylation of 4-aminodiphenyl ether with dimethyl sulfate in aqueous $NaHCO_3$ solution as described by Evans[27]. 4-Aminodiphenyl ether was prepared by the reduction of 4-nitrodiphenyl ether with zinc dust as described by Suter.[28] 4-Chloro-*N,N*-dimethylaniline and 3-chloro-*N,N*-dimethylaniline were prepared by the usual methylation of *p*-chloro- and *m*-chloroanilines with dimethyl sulfate in dioxane. Distillation gave crude products, which were then purified through an alumina column chromatography with *n*-hexane in order to remove trace amount of secondary and primary amines and finally distilled. *N,N,N',N'*-tetramethyl-*p*-phenylenediamine was prepared as follows.[29] A mixture of 8 g of hydrochloric acid and 8 g of methanol was placed in a sealed tube and heated at 180—200°C for 3 hr. After breaking the tube, the reaction mixture was poured into a sufficient amount of 10% aqueous sodium hydroxide solution to afford a precipitate, which was then filtered and washed several times with water, dried and finally recrystallized from *n*-hexane. Mp 49—50. Yield 50%.

Substituted Phenyl Methyl Sulfones. *p*-Chloro-, *m*-chloro-, *p*-phenoxyphenyl methyl sulfones and unsubstituted phenyl methyl sulfone were prepared by the oxidation of the corresponding sulfides with an execess amount of hydrogen peroxide in acetic acid and recrystallized twice from benzene-*n*-hexane.

Other α-Substituted Compounds. Ethanedithioformal, diethylthioformal, diphenylthioformal and diphenylformal were prepared by the substitution reaction of methylene chloride with corresponding sodium mercaptides and phenoxide in ethanol. After the usual work-up, ethanedithioformal, diethylthioformal, and diphenylformal were distilled under reduced pressure through an efficient column. Diphenylthioformal was recrystallized from petroleum ether. Tris(phenylmercapto) methane was prepared by the substitution reaction of ethyl orthoformate with thiophenol in benzene using boron trifluoride as a catalyst and recrystallized from methanol to give colorless crystals melting at 39—40°C.

Di-t-butyl peroxide. Di-*t*-butyl peroxide was prepared by Milas and Surgenor's method.[30] This peroxide was distilled to give distillate boiling at 109—110°C. No detectable amount of *t*-butyl hydroperoxide was found to be contained from the IR and NMR spectra.

Elemental analysis. Found: C, 65.35; H, 12.30% Calcd: C, 65.70, H, 12.40%.

Deuterated Thioanisole. Thioanisole 2.0 g (*ca.* 0.016 mol) was poured into 12.5 g (*ca.* 0.12 mol) of *t*-BuOD (70% deuterated) containing 0.6 g (*ca.* 0.012 mol) of metal potassium and the mixture was sealed into an ampoule ***in vacuo***, which was kept at 90°C for 48 hr. The usual work-up gave 1.8 g of 33% deuterated thioanisole by NMR measurement.

Chlorobenzene. Chlorobezene used for solvent was purified by washing commercial grade of chlorobenzene with concentrated sulfuric acid, and then distillation over phosphorus pentoxide. The distillate was distilled again through an efficient column. Bp 130.5—131.0°C. Purities of all the substrates used in this experiment were carefully checked by IR, NMR, Gas chromatography and elemental analyses. Properties of all these compounds used

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[23] H. Gilmann and G. C. Gainer, *J. Am. Chem. Soc.*, **71**, 1749 (1949).

[24] E. Miller, F.S.Crossley and M.L.Moore, *ibid.*, **64**, 2322 (1942).

[25] E. Goethals and P. de Radgitzky, *Bull. Soc. Chem. Belges.*, **73**, 546 (1964).

[26] R.Q.Brewster and T.Groening, "Org. Syntheses," Coll. Vol. II, p. 445 (1943).

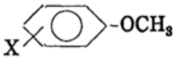
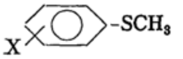
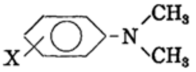
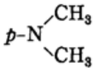
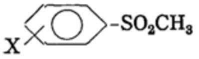
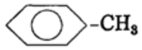
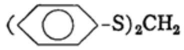
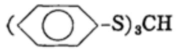
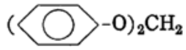
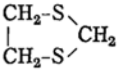
[27] D.P. Evans and R. Williano, *J. Chem. Soc.*, **1939**, 1199.

[28] C.M.Suter, *J. Am. Chem. Soc.*, **51**, 2581 (1929).

[29] C. Wurster, *Ber.*, **12**, 526 (1879).

[30] N.A. Milas and D.M. Surgenor, *J. Am. Chem. Soc.*, **68**, 205, 643 (1946).

TABLE 7. THE MELTING AND BOILING POINTS, ELEMENTAL ANALYSES AND CHEM. SHIFT OF α-PROTON OF SUBSTRATES USED IN THIS EXPERIMENT

Compound	Bp °C/mmHg (mp °C)	Elemental analysis Found (C, H)	Elemental analysis Calcd (C, H)	Chem. shift[a] (ppm)
				
X = H	155—155.5			
p-Cl	98.5—98.7/30			3.73
m-Cl	114.5—115/65			
p-CH_3O	(78—79)			
m-CH_3O	91.5—92.5/12			
p-CN	(59—60)	72.00, 5.13	72.16, 5.30	
				
H	93.2—93.5/31.5			2.42
p-Cl	94.4/2			
m-Cl	90.5—91/1.5			
p-CH_3O	132/24			
p-CH_3	110/29			
p-PhO	172—173/2			
p-CN	(63—64)	64.53, 4.65	64.39, 4.73	
				
H	100—1.005/40			2.88
p-Cl	85/5(32)			2.88
m-Cl	76/1.5			2.89
p-PhO	152—153/5	79.16, 7.22	78.84, 7.09	2.89
 p-$N(CH_3)_2$	(49—50	73.35, 9.84	73.12, 9.82	2.79
p-CN	(73—74)	74.13, 6.99	73.94, 6.90	3.01
				
H	(88.5—89.2)			2.94
p-Cl	(96—97)			2.95
m-Cl	(108—109.5)			2.96
p-PhO	(85—86)			2.92
	110.3—110.7			2.33
	(36—37)			4.24
	(39.4—39.8)	67.09, 4.70	67.01, 4.74	5.30
	121—122/1.6			5.67
$C_2H_5SC_2H_5$	91.3—91.5			
$(C_2H_5S)_2CH_2$	96.0—96.5/45	43.62, 8.54	44.12, 8.82	3.70
 CH_2-S-CH_2-S-CH_2	8.5—86/53	33.65, 5.63	33.96, 5.66	3.89

a) In 10 % CCl_4, TMS was used as an internal standard.

for kinetics are listed in Table 7.

Kinetic Procedure. Each sample substrate was weighed in a 5 m*l* volumetric flask and diluted with chlorobenzene to make the total volume of the solution exactly 5 m*l*. The solution, 2 m*l* was pipetted out into a glass tube (*ca.* 10 m*l* volume), into which 2 m*l* of 0.214 M of di-*t*-butyl peroxide-chlorobenzene solution was pipetted to make the total volume of 4 m*l*. The tube was cooled with dry ice-acetone, evacuated three times and sealed. The tubes were set in a paraffin bath kept at 130 ±0.5°C for 42 hr.

The cooled tube was opened, into which 1 m*l* of toluene solution containing 0.74 mmol of benzene per 1 ml was added for the internal standard of gas chromatography. The mixture in the tube was placed in a distilling flask and distilled. The distillate below 130°C was collected and the amounts of acetone and t-butanol were analyzed by gas chromatography using PEG 6000 4 m column at 81°C using hydrogen as a carrier gas. From the relative areas of two peaks, the moles of acetone and t-butanol produced in the reaction were calculated using the calibration line.

Values of k_a/k_d were calculated by Eq. (6).