TRANSFER OF d-ORBITAL CONJUGATION OF SULFUR THROUGH A BENZENE RING

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Teoreticheskaya i Eksperimental'naya Khimiya, Vol. 5, no. 2, pp. 191–195, 1969

UDC 547.73

The rate constants for deuterium exchange with liquid NH_3 have been measured for CD_3S groups in isomers of methoxythioanisole (I–III) and for CD_3 groups in p-methylthioanisole (IV) and di-p-tolyl sulfide (V). The catalyst was potassium amide. There is found to be conjugation involving the d orbitals of the sulfur atom and the electrons in the second substituent, which is transmitted via the benzene ring in the ground state for I–III and in the transition states for protophilic deuterium exchange in IV and V. The d-orbital conjugation in organosulfur compounds is compared with that in organophosphorus ones.

We have shown [1] that d-orbital conjugation in an aralkyl sulfide is transmitted through the benzene ring if the para position of the latter carries a dimethylamino group, which is a vigorous electron donor. This gives the S-atom in p-dimethylaminothioanisole a negative charge, while the N-atom carries the excess positive charge. This makes itself felt [2] in that the dipole moment of this compound is greater than that calculated by vector addition of the group moments. One consequence of this charge distribution is that there is a reduced rate of exchange of D between liquid ammonia and CD_3S groups with KNH_2 as catalyst (relative to unsubstituted thioanisole), while the $(CH_3)_2N$ group shows more rapid exchange than does that in dimethylaniline.

Table 1

Rate Constants for Exchange Between Liquid Ammonia and SCD_3 Groups in Thioanisole and Isomers of Methoxythioanisole (0.02 M KNH_2, −60° C)

Compound	k, sec^{-1}
Thioanisole	2,3 (±0,4) 10^{-3}
Ortho isomer	6.2 (±0.6) 10^{-4}
Meta isomer	4.5 (±0.6) 10^{-3}
Para isomer	9.0 (±0.8) 10^{-4}

We have examined how the d-orbital conjugation is affected if $N(CH_3)_2$ is replaced by OCH_3, which is a weaker electron donor. For this purpose we examined deuterium exchange in CD_3S for isomers of methoxythioanisole.

A methyl group is even weaker as an electron donor than is an OCH_3 group. The dipole moment [3] indicates that d-orbital conjugation is absent in methylthioanisole.

On the other hand, hydrogen in a methyl group is protonated much more easily than that in OCH_3 or $N(CH_3)_2$ as is clear [1, 4, 5] from the relative rates of exchange with liquid ammonia for those groups as substituents in benzene rings:

$N(CH_3)_2$	OCH_3	CH_3
1	30	10 000

Hydrogen in a methyl group is relatively easily protonated, so we have examined whether a benzene ring transmits conjugation between the vacant d-orbitals of sulfur and the electrons of the benzyl carbanion produced during deuterium exchange between a strong base and the CH_3 group in p-methylthioanisole. Electron delocalization stabilizes the carbanion, so we expect elevated mobility in the CH_3 hydrogen and hence accelerated exchange relative to CH_3 in toluene.

If this effect actually occurs, it should be accentuated when the sulfur atom is linked not to a CH_3 group in SCH_3 but to a second phenyl group, which increases the electron-acceptor capacity of the sulfur atom. We know [5, 7] that increase in the positive charge on the S atom elevates the capacity for electron-acceptor conjugation. We have, therefore, compared the rates of deuterium exchange in CH_3 groups for toluene and di-p-tolyl sulfide.

RESULTS AND DISCUSSION

Methoxythioanisole. We used 0.02 M KNH_2 at −60° C in liquid NH_3. Table 1 gives the mean rate constants.

The exchange is slow in the ortho and para isomers, but the rate reduction in the p isomer is less by a factor of 40 than that in p-dimethylaminothioanisole, on account of the less marked electron-donor behavior of the OCH_3 group. The accelerated exchange in SCD_3 for the meta isomer occurs because an OCH_3 group draws off electrons by induction.

Table 2

Rate Constants for Exchange Between Liquid Ammonia and CD_3 Groups in Toluene and Other Compounds (0.02 M KNH_2, 0° C)

Compound	k, sec^{-1}	k_{rel} (CD_3)
Toluene	5,0 (±0.4)·10^{-4}	1,0
p-Methylthioanisole	1,0 (±0,15)·10^{-3}	2,0
Di-p-tolyl sulfide	7.0 (±0.8)·10^{-3}	14
Methyl p-cresyl ether	—	0.17

Conjugation exists in the ortho and para isomers of methoxythioanisole, as is clear [7] from comparison with deuterium exchange in the isomeric dimethoxy-

Table 3

Deuterium Exchange in Thioanisole and Isomers of Methoxythioanisole (0.02 M KNH_2, −60° C)

τ, min	C_τ	k, sec⁻¹	τ, min	C_τ	k, sec⁻¹
o-$OCH_3C_6H_4SCD_3$; C_0= 2.37 at. % D			p-$OCH_3C_6H_4SCD_3$; C_0= 1.89 at. % D		
10	1.52	$7.5\cdot10^{-4}$	10	1,05	$9.8\cdot10^{-4}$
10	1.74	$5.2\cdot10^{-4}$	15	0.81	$9.4\cdot10^{-4}$
10	1.63	$6,2\cdot10^{-4}$	15	0.96	$7.5\cdot10^{-4}$
20	1.16	$6,0\cdot10^{-4}$	20	0.62	$9.3\cdot10^{-4}$
m-$OCH_3C_6H_4SCD_3$; C_0= 2.27 at. % D			$C_6H_5SCD_3$; C_0= 2.74 at. % D		
3	0.91	$5.1\cdot10^{-3}$	5	1.69	$1.6\cdot10^{-3}$
3	1.07	$4.2\cdot10^{-3}$	6	1,01	$2.8\cdot10^{-3}$
4	1.07	$3.2\cdot10^{-3}$	6	1.06	$2.6\cdot10^{-3}$
4	0.77	$4,5\cdot10^{-3}$	7	0.43	$2.2\cdot10^{-3}$
5	0.43	$5.5\cdot10^{-3}$			

τ = run duration, C_τ = deuterium concentration in water from combustion at end.

benzenes, where such an effect is impossible. The following are the results for $k_{rel}(SCD_3)$ and $k_{rel}(OCD_3)$, the ratios of the exchange rates for 1) methoxythioanisole and thioanisole; and 2) dimethoxybenzene and anisole:

	o	p	m
k_{rel} (SCD_3)	0,27	1,90	0,39
k_{rel} (OCD_3)	2,10	0,90	0,42

The dimethoxybenzene isomers show a monotonic fall in k as the two OCH_3 groups become further apart. The reactivity difference between methoxythioanisole and dimethoxybenzene is naturally ascribed to differing effects of the OCH_3 group on the mobility of hydrogen in SCH_3 and OCH_3 in the ortho and para positions; in the first case there is p-d conjugation in the ground state, while in the second the OCH_3 group has a negative inductive effect.

Para-methylthioanisole and di-p-tolyl sulfide. Table 2 gives the mean exchange rate constants for CH_3 in toluene and these two compounds measured with 0.02 M KNH_2 at 0° C with the corrections described in the experimental section.

Table 4

Deuterium Exchange of p-Methylthioanisole (C_{KNH_2} = 0.02 M; 0° C; C_0 = 4.09 at. % D)

τ	C_τ	k, sec⁻¹
10	2.43	$9\cdot10^{-4}$
15	1.31	$13\cdot10^{-4}$
16	1.79	$9\cdot10^{-4}$
20	1.19	$10\cdot10^{-4}$

Table 2 shows that D in the methyl group of p-methylthioanisole exchanges more rapidly than that in toluene, although only by a factor of 2. However, this clearly is due to d-orbital conjugation of the S atom, because replacement of S by O (in methyl p-cresyl ether [8]) retards the exchange in the methyl group relative to that in toluene, and $k_{rel}(CD_3)$ = 0.17. Also, D in methyl in di-p-tolyl sulfide exchanges seven times more rapidly than that in p-methylthioanisole.

Table 5

Deuterium Exchange of Di-p-tolyl Sulfide (C_{KNH_2} = 0.02 M; 0° C; C_0 = = 1.81 at. % D)

τ	C_τ	k, sec⁻¹
8	0.77	$1.8\cdot10^{-3}$
8	0.79	$1,7\cdot10^{-3}$
12	0.47	$1.9\cdot10^{-3}$

These results are especially interesting in relation to hydrogen exchange [9, 10] in the para and meta isomers of organophosphorus compounds: tolyldiphenylphosphine and tolyldiphenylphosphine oxide. The rates of exchange of the CH_3 group with t-butanol, as catalyzed by potassium t-butoxide, are in the ratio 25 for the para and meta isomers of the first compound (P trivalent), while in the second (P pentavalent) the ratio is 200. The phosphorus d-orbitals are thus involved in conjugation with the electrons of the carbanion in the transition state of the exchange reaction with the base.

Sulfur and phosphorus (third-period elements) thus show conjugation involving participation of the vacant d-orbitals and the electrons of the second substituent, which is transmitted through the benzene ring in the ground state and in the transition state of protophilic hydrogen exchange, whereas O and N (second-period elements) do not show this effect.

EXPERIMENTAL

The following are the conditions of synthesis. Tne purities were checked by V. M. Basmanova by gas-liquid chromatography.

1. o-Methoxythioanisole. $o\text{-}H_2NC_6H_4OCH_3 \xrightarrow[\substack{\text{2. } KSC(S)OC_2H_5 \\ \text{3. } KOH,\ C_2H_5OH}]{\text{1. } HCl,\ NaNO_2\ [11]}$

$\longrightarrow o\text{-}HSC_6H_4OCH_3 \xrightarrow{CD_3I\ [12]}$

$\longrightarrow o\text{-}CD_3SC_6H_4OCH_3 \cdot (n_D^{21}\ 1{,}5856;\ n_D^{20}\ 1{,}5870)$*.

2. m-Methoxythioanisole. $m\text{-}H_2NC_6H_4OCH_3 \longrightarrow$

$\xrightarrow{[11]} m\text{-}HSC_6H_4OCH_3 \xrightarrow{(CD_3)_2SO_4[13]}$

$\longrightarrow m\text{-}CD_3SC_6H_4OCH_3 \cdot (n_D^{20} 1.5822)$*.

3. p-Methoxythioanisole. $p\text{-}H_2NC_6H_4OCH_3 \xrightarrow{[11]} p\text{-}HSC_6H_4OCH_3 \longrightarrow$

$\xrightarrow{[13]} p\text{-}CD_3SC_6H_4OCH_3.\ (n_D^{22}\ 1{,}5780)$*.

4. p-Methylthioanisole. A. $p\text{-}H_2NC_6H_4CH_3 \xrightarrow{[11]} p\text{-}HSC_6H_4CH_3 \longrightarrow$

$\xrightarrow{[13]} p\text{-}CH_3SC_6H_4CH_3.\ (n_D^{20} 1{,}5745)$; B. $p\text{-}H_2NC_6H_4Br \longrightarrow$

$\xrightarrow[\text{2. } KSC\ (S)OC_2H_5]{\text{1. } NaNO_2,\ HCl\ [14]} p\text{-}HSC_6H_4Br \xrightarrow{[13]} p\text{-}CH_3SC_6H_4Br \longrightarrow$

$\xrightarrow[\text{2. } (CD_3)_2SO_4]{\text{1. } Mg\ [15]} p\text{-}CH_3SC_6H_4CD_3.$

The final material contained 23% of undeuterated thioanisole. No other impurities were detected by gas-liquid chromatography.

5. Di-p-tolyl sulfide. A. $p\text{-}H_2NC_6H_4CH_3 \xrightarrow[\text{2. } Na_2S]{\text{1. } NaNO_2,\ HCl\ [16]}$

$\longrightarrow (CH_3C_6H_4)_2S \cdot (\text{mp } 56{,}0 - 56{,}5°)$; B. $C_6H_5CH_2Cl \xrightarrow[\text{2. } D_2O]{\text{1. } Mg}$

$\longrightarrow C_6H_5CH_2D \xrightarrow{HNO_3 + H_2SO_4} p\text{-}O_2NC_6H_4CH_2D \xrightarrow{Sn + HCl}$

$\longrightarrow p\text{-}H_2NC_6H_4CH_2D \xrightarrow{[16]} (DCH_2C_6H_4)_2S \cdot (\text{mp } 55{,}5 - 56{,}5°).$

These two di-p-tolyl sulfide specimens gave dark-blue solutions in liquid ammonia [17] on account of the presence of a little elemental sulfur, which can arise by oxidation of Na_2S in the last stage of the synthesis.

The exchange was performed in a two-armed reaction vessel [18]. The reaction was stopped by addition of NH_4Cl, and the compound was extracted with ether. The ethereal solution was dried, and the compound was isolated and distilled; then the compound was burned to produce water, whose deuterium content was measured (C_0, at. %). We used 900-1800 moles of NH_3 per mole of compound. All the compounds were chemically stable in solutions of KNH_2 in ammonia. Table 3 gives the results with thioanisole and isomers of methoxythioanisole.

Various checks were required in order to obtain reliable deuterium exchange rate constants for the methyl groups of p-methylthioanisole (III) and di-p-tolyl sulfide (IV). Gas-liquid chromatography showed that the composition of preparation III (77% $CH_3SC_6H_4CD_3$ + 23% $C_6H_5SCH_3$) was virtually unaltered by the exchange.

The solution of III in liquid ammonia in the presence of KNH_2 is orange-red, which points to partial consumption of KNH_2, which undoubtedly occurs with IV, since the amide reacts with sulfur in liquid ammonia [19]. To determine the true KNH_2 concentration in the experiments with III and IV, we added $C_6H_5CH_2D$ or $C_6H_5SCD_3$ to solutions of these compounds of ordinary isotopic composition, since the exchange rate constants for these compounds had been determined separately. We found that compound III did not affect the exchange rate constants for deuterotoluene and deuterothioanisole, so the color in the solution of compound III is not associated with a reduction in the concentration of KNH_2, and the results for p-methylthioanisole (Table 4) may be taken without correction.

On the other hand, di-p-tolyl sulfide reduced the rate of exchange in deuterotoluene by a factor 4, so the mean rate constant of $1.8 \pm 0.1 \cdot 10^{-3}$ for IV (Table 5) must be increased by a factor of 4 to $k = 7 \cdot 10^{-3}$ sec^{-1}, which is 14 times the value for toluene.

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5 January 1968

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*The purity was also checked by microanalysis.