Tetrahedron. Vol. 25, pp 2749 to 2755 Pergamon Press 1969. Printed in Great Britain

DEUTEROEXCHANGE STUDY OF 3d ORBITAL CONJUGATION IN ORGANIC SULFIDES

A. I. SHATENSHTEIN and H. A. GVOZDEVA
L. YA. Karpov Institute of Physical Chemistry, Moscow, USSR

(Received in the UK 20 *November* 1968; *Accepted for publication* 16 *December* 1968)

Abstract—The kinetics of dedeuteration under the action of potassium amide in liquid ammonia in a series of sulfides with open chain, open chain–alicyclic and open chain–aromatic substituents and a number of their oxygen analogs have been determined to investigate the electronic effect of 3d orbital conjugation in divalent sulfur compounds. The conjugation of the 3d orbitals of sulfur has been studied (1) with the adjacent, negatively charged carbon electrons of the intermediate carbanion; (2) with a pair of unshared electrons of the substituent (OMe, $N(Me_2)$; *via* the benzene ring) in the ground state of the sulfide molecule; (3) with the charge (*via* the benzene ring) in the intermediate anion formed in the exchange reaction. (4) In addition hyperconjugation of the type $—\bar{S}{=}CH_2H^+$ has been investigated.

THE present work deals with the participation of the vacant 3d orbitals of divalent sulfur in conjugative interaction. The existence of such interaction in the ground, excited and transition states of sulfides has been refuted by a number of authors. However, convincing evidence has been forwarded as proof of the existence of this effect (see reviews[1–3]). The electron-accepting ability of the S atom, particularly, comes to the fore when a strong electron-releasing centre is present in the sulfide, for instance, a negatively charged C atom attached to sulfur in the carbanion intermediate, such as is formed in protophilic hydrogen isotope exchange. The measurement of the rate of this reaction is a convenient method for the quantitative study of d orbital conjugation.[4, 5] As a rule, in the study[4–8] of this effect, compounds with several divalent sulfur atoms in the molecule previously were used, so that the observed effect was the result of the combined action of more than one S atom. By using a highly protophilic system (solution of potassium amide in liquid ammonia[9–11]) we have been able to measure[12–16] the kinetics of the hydrogen isotopic exchange in sulfides of low reactivity and thus have obtained novel results relating to conjugation of the d orbital of the S atom.

In most cases, the rate of dedeuteration of a substance, with a deuterium atom previously introduced into a given position of the molecule, was determined. In order to estimate the reactivity of nonequivalent C—D bonds, the ratio f of the deuterium exchange rate constant for a given C—D bond in the compound considered was compared with that for the C—D bond in benzene measured under similar conditions.

The following is a comparison of f values determined in our laboratory for Me groups bound to a benzene ring by means of sulfur,[12, 13] selenium,[17] oxygen,[18] phosphorus,[19] or nitrogen.[14]

	f	$f_{rel.}$
$C_6H_5SCH_3$	1×10^6	2×10^8
$C_6H_5SeCH_3$	1×10^5	2×10^7
$C_6H_5OCH_3$	0·22	4×10^1
$C_6H_5P(CH_3)_2$	140	3×10^4
$C_6H_5N(CH_3)_2$	0·005	1

This clearly shows the considerable increase in hydrogen mobility of a C—H bond, in the vicinity of an element (S, Se or P) possessing vacant d-orbitals energetically close to the valency electron orbitals, (as compared with an element—O or N) in which the valency shell can expand to a decet so that their atoms can participate in electron-accepting conjugation for instance:

$$-\mathrm{S}-\overset{\ominus}{\underset{|}{\mathrm{C}}}- \longrightarrow -\overset{\ominus}{\mathrm{S}}=\underset{|}{\mathrm{C}}-$$

In the exchange reaction of thioanisole not only the vacant 3d orbitals of the S atom, but also the π-electron system of the benzene ring participate in transmission of the charge of the intermediate carbanion. This is substantiated by introducing a methylene group between the benzene ring and the S atom (as in benzyl methyl sulfide[16]) which disrupts the conjugative interaction with the benzene ring, resulting in an abrupt fall in the rate of hydrogen isotope exchange of the Me group.[14]

	f
$C_6H_5SCH_3$	10^6
$C_6H_5CH_2SCH_3$	~ 2
CH_3SCH_3	~ 3

Since alicyclic substituents, as a rule, are more energetic electron-donors than the Me group (cf., for instance, the inductive σ_* constants and other data[14]) it was surprising that the rate of hydrogen exchange in the Me groups of methyl cyclopentyl and methyl cyclohexyl sulfides[14] is higher by two orders of magnitude than in dimethyl sufides.

	f
CH_3SCH_3	~ 3
$C_5H_9SCH_3$	550
$C_6H_{11}SCH_3$	600

The lower rate in dimethyl sulfide is perhaps due to hyperconjugation of the type $\mathrm{Me_3{-}\overset{\ominus}{S}{=}CH_2\overset{\ominus}{H}}$ (see 8) in which the negative charge on the S atom impairs its ability to accept electrons from the negatively charged substituent in the intermediate of the protophilic hydrogen exchange reaction. The lower rate due to this effect should be greater when the S atom is attached to a primary C atom as in dimethyl sulfide than when it is attached to a secondary C atom as in methyl cycloalkyl sulfides. It was found that in methyl t-butyl sulfide,[16] where this hyperconjugation effect is excluded, the rate of exchange in the Me group is increased by an order of magnitude of a Me group of dimethyl sulfide although the positive inductive effect of a t-Bu group is greater than that of a Me group.

	f
t-$(CH_3)_3CSCH_3$	~ 40
CH_3SCH_3	~ 3

This therefore is additional evidence that the hyperconjugation effect accelerates the exchange reaction of methyl cyclopentyl and methyl cyclohexyl sulfides as compared with dimethyl sulfide, although it is not the only contributing factor (see 14).

The acidity of the open chain—aromatic sulfide changes as first one and then two hydrogen atoms in the methyl mercapto group of thioanisole are substituted by Me groups. The carbanion stability decreases in the order primary > secondary > tertiary, since substitution of hydrogen by the electron-donating alkyl group increases the negative charge on the C atom so that removal of a proton from it requires an ever increasing amount of energy. Therefore, the hydrogen exchange rate in the α-position is lower in ethylbenzene than in toluene and is still lower in isopropylbenzene:[20]

	f
$C_6H_5CH_3$	70
$C_6H_5CH_2CH_3$	10
$C_6H_5CH(CH_3)_2$	2

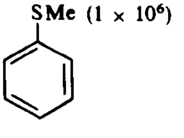
This phenomenon is more pronounced in the case of sulfides:[12, 14]

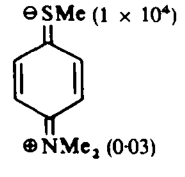
	f
$C_6H_5SCH_3$	10^6
$C_6H_5SCH_2CH_3$	10^4
$C_6H_5SCH(CH_3)_2$	10^2

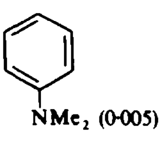
When the intermediate carbanion is stabilized by the conjugation of its electrons with the 3d orbitals of several S atoms the mobility of the α-carbon hydrogens is so increased that the rate of exchange of thioacetal $(C_6H_5S)_2CH_2$ and of orthothioformate $(C_6H_5S)_3CH$ in liquid ammonia can be measured without a catalyst[14] (cf. 5, 7).

The hydrogen isotope exchange method not only permits a quantitative study of 3d orbital conjugation with an anion centre ajacent to the S atom, but also of the transmission of the electron effect via the π-electron system of the benzene ring. This occurs when the latter possesses a sufficiently energetic electron-donating *para* or *ortho* substituent as can be seen from the following examples.

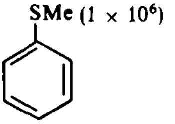
The dipole moment of *p*-dimethylaminothioanisole has been shown[21] to exceed by 0·58D the value calculated from additivity of the group moments, apparently due to the conjugation between the nitrogen lone electron pair of the dimethylamino group and the vacant 3d orbitals of the methylmercapto sulfur. In the ground state of the molecule the S atom is negatively charged while the N atom possesses a positive charge. This explains the lowered tendency of the S atom to participate in electron-accepting conjugation with an anion centre of the exchange intermediate with the resultant fall in rate of deuteroexchange in the SCD_3-group to 1/100 that of thioanisol.[14] Deuteroexchange rate in the $N(CD_3)_2$-group of *p*-dimethylaminothioanisole proceeds 6 times faster than in unsubstituted dimethylaniline owing to the inductive shift of electrons of the dimethylamino C—D bonds towards to positively charged N atom. The f values are given alongside the formulas

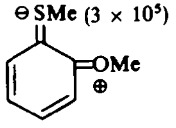


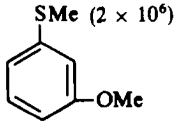


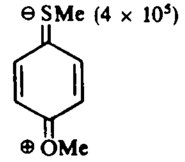


If the dimethylamino group is substituted by a weaker electron-donating methoxy-group, it was found[15] that in the SCD_3-group of the *ortho* and *para* isomers the exchange rate is $\frac{1}{4}$ that of thioanisole and $\frac{1}{40}$ that of *p*-dimethylaminothioanisole. In the SCD_3-group of the *meta* isomer the reaction rate is twice that of thioanisole, apparently due to the inductive electron shift towards the OMe group

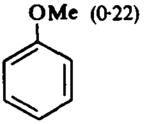


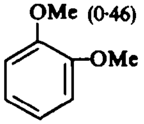


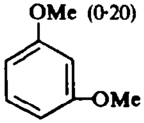


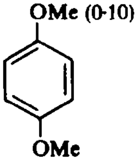


In the oxygen analogs, i.e. in dimethoxybenzene isomers, *d*-orbital conjugation is excluded and[18] a monotonic decrease is observed in the relative exchange rate with increasing distance between the OMe substituents (if the deutero-exchange rate constant in the OMe group of anisole is taken as unity, in *ortho* dimethoxybenzene it is 2·0, in *meta* 1·0 and in *para* 0·4).





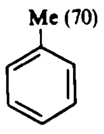


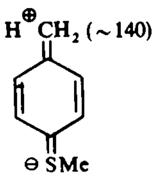


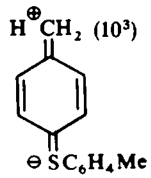
As the Me group is a still weaker electron-donor than the OMe group, it follows from the results of dipole moment measurements[22] that 3d orbital conjugation in the ground state of *p*-methylthioanisole molecule is absent. However, the potassium amide catalyzed reaction in liquid ammonia showed that the proton of the Me group of toluene is more easily removed by the base than in the $N(Me)_2$ and OMe-groups[18, 20, 23]

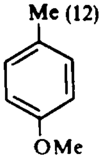
NMe_2	OMe	Me
1	30	10000

It was decided to see whether conjugative interaction between the sulfur *d*-orbitals and the benzyl carbanion electrons of the exchange intermediate in the reaction between the Me group of *p*-methylthioanisole and a strong base can accur via the benzene ring. Since the benzyl carbanion is stabilized by electron delocalization we may expect an acceleration of the hydrogen exchange rate in the Me group of the compounds mentioned as compared with the same group in toluene. If the expected effect does exist it should become stronger when the S atom is linked not with an electron-donating Me group to form SMe, but with a second Ph group which augments its electron-accepting properties. It is known from the literature[24, 25] that augmentation of the positive charge on the S atom increases its capacity to participate in electron-accepting conjugation. We therefore also compared the deuteroexchange rates of the Me groups in di-*p*-tolysulfide and toluene. The *f* values obtained are given alongside the formulas









Indeed, in experiments with *p*-methylthioanisole[15] the reaction rate was found to be twice that for toluene whereas our data obtained for the oxygen analogs, i.e. for the methyl *p*-cresolate, showed the exchange rate for the Me group of this compound to be only ⅙ that for the Me of toluene, while di-*p*-tolylsulfide showed a 14-fold increase in the rate.

EXPERIMENTAL

The experiments with solutions of potassium amide in liquid ammonia were carried out as reported.[11,26] The deuterium concentration in the water resulting from combustion of the substance was determined by the drop method.[27] The constants of the substances or of their GLC characteristics were practically identical before and after the runs. For calculating *f* we used the values of the deuterium exchange rate constants of benzene listed in Table 1.

TABLE 1. RATE CONSTANTS POTASSIUM AMIDE CATALYZED DEUTERIUM EXCHANGE OF BENZENE IN LIQUID AMMONIA.

t°C	Concentrations of KNH_2 (C_{KNH_2}, N)			
	0·01	0·02	0·06	0·43
−60	(1×10^{-9})	(2×10^{-9})	—	—
−30	(1×10^{-7})	(2×10^{-7})	4×10^{-7}	—
0	4×10^{-6}	7×10^{-6}	(2×10^{-5})	9×10^{-5}
25	$4{\cdot}4 \times 10^{-5}$	$8{\cdot}6 \times 10^{-5}$	$1{\cdot}8 \times 10^{-4}$	—

The figures in parentheses are for values of the constants calculated according to the equation in Ref. 9, p. 104.

Table 2 shows the mean values of the isotope exchange rate constants (sec^{-1}).

TABLE 2. RESULTS OF THE DEUTERIUM EXCHANGE EXPERIMENTS

Substances	C_{KNH_2}	t	k	f	References
$C_6H_5SCD_3$	0·01	−60	1×10^{-3}	1×10^{6}	13
	0·02	−60	2×10^{-3}	1×10^{6}	15
$C_6H_5SeCD_3$	0·02	−60	2×10^{-4}	1×10^{5}	17
$C_6H_5OCD_3$	0·06	25	$4{\cdot}0 \times 10^{-5}$	$2{\cdot}2 \times 10^{-1}$	18
$C_6H_5N(CD_3)_2$	0·06	25	$9{\cdot}0 \times 10^{-7}$	5×10^{-3}	14
$C_6H_5CH_2SCD_3$	0·45	0	$1{\cdot}6 \times 10^{-4}$	~2	16
CH_3SCH_3	0·45	0	$3{\cdot}0 \times 10^{-4}$	~3	14
$C_5H_9SCD_3$	0·06	−30	$2{\cdot}4 \times 10^{-4}$	$6{\cdot}0 \times 10^{2}$	14
$C_6H_{11}SCD_3$	0·06	−30	$2{\cdot}2 \times 10^{-4}$	$5{\cdot}5 \times 10^{2}$	14
t-$(CH_3)_3CSCH_3$	0·06	0	$6{\cdot}7 \times 10^{-4}$	~40	16
$C_6H_5SCD_2CH_3$	0·06	−60	$1{\cdot}4 \times 10^{-4}$	3×10^{4}	14
$C_6H_5SCD(CH_3)_2$	0·06	−30	$3{\cdot}0 \times 10^{-5}$	1×10^{2}	12
$(C_6H_5S)_2CH_2$	*	120	$6{\cdot}0 \times 10^{-6}$	—	14
$(C_6H_5S)_3CH$	*	120	$2{\cdot}0 \times 10^{-6}$	—	14
p-$(CH_3)_2NC_6H_4SCD_3$	0·02	−30	3×10^{-3}	1×10^{4}	14
p-$(CD_3)_2NC_6H_4SCH_3$	0·06	25	6×10^{-6}	3×10^{-2}	14
o-$CH_3OC_6H_4SCD_3$	0·02	−60	6×10^{-4}	3×10^{5}	15
m-$CH_3OC_6H_4SCD_3$	0·02	−60	5×10^{-3}	2×10^{6}	15
p-$CH_3OC_6H_4SCD_3$	0·02	−60	9×10^{-4}	4×10^{5}	15
o-$CD_3OC_6H_4OCD_3$	0·06	25	$8{\cdot}3 \times 10^{-5}$	$4{\cdot}6 \times 10^{-1}$	18
m-$CD_3OC_6H_4OCD_3$	0·06	25	$3{\cdot}6 \times 10^{-5}$	$2{\cdot}0 \times 10^{-1}$	18
p-$CD_3OC_6H_4OCD_3$	0·06	25	$1{\cdot}7 \times 10^{-5}$	$1{\cdot}0 \times 10^{-1}$	18
p-$CH_3SC_6H_4CD_3$	0·02	0	$1{\cdot}0 \times 10^{-3}$	~$1{\cdot}4 \times 10^{2}$	15
(*p*-$CD_3C_6H_4)_2S$	0·02	0	$7{\cdot}0 \times 10^{-3}$	~$1{\cdot}0 \times 10^{3}$	15

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* Runs were made in liquid ammonia without catalyst.

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