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Abstract

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STUDY OF THE EFFECT OF SOLVENT ON THE POSITION OF TAUTOMERIC EQUILIBRIUM IN A SERIES OF ARYL THIOCARBAZONES

(Presented by Academician B. A. Kazanskii, 27 XII 1957)

The effect of solvent on the position of tautomeric equilibrium is generally known. However, many questions in the theory of this phenomenon have until recently remained unclear. In recent years much has been done in this direction by M. I. Kabachnik and co-workers ([1–6]).

In generalized form these questions have been considered by A. N. Nesmeyanov and M. I. Kabachnik ([7–10]).

M. I. Kabachnik ([1]) applied the modern theory of acid–base equilibrium, developed by Brønsted ([11]) and N. A. Izmailov ([12]), to the calculation of tautomeric equilibrium. Kabachnik derived a formula expressing the dependence between the constants of tautomeric equilibrium in two solvents: S_1 and S_2

$$pK_{\mathrm{TS2}} = pK_{\mathrm{TS1}} + \mathrm{const.} \tag{1}$$

If pK_{TS} in two solvents is plotted along the coordinate axes, then for all keto-enols the points on the graph should lie on one straight line with a slope tangent equal to 1. Upon verification it was confirmed that the derived relation is valid for many keto-enols ([10]). Recently M. I. Kabachnik and co-workers showed that relation (1) is valid for tautomeric equilibrium in a series of dialkyl thiophosphates ([6]). It is of interest to verify whether relation (1) is applicable to tautomeric equilibrium in the series of aryl thiocarbazones.

One of us ([13]) showed that 1,5-diphenylthiocarbazone (dithizone) in solvents is a mixture of the tautomers thione (a) and thiol (b):

$C_6H_5N{=}N$ $\quad$ $C_6H_5N{=}N$
\ $\quad$ \
$C{=}S$ $\quad$ $C{-}SH$
/ $\quad$ ‖
C_6H_5NHNH $\quad$ $C_6H_5NH{-}N$

a *b*

The ratio of thione and thiol forms in the tautomeric mixture depends on the nature of the solvent and of the substituent in the aromatic rings of the thiocarbazone. It was shown that the short-wave maximum ($\lambda_{\max 1}$) on the absorption-spectrum curve, 450 mμ, belongs to the thiol form, while the absorption maximum 620 mμ ($\lambda_{\max 2}$) belongs to the thione form of dithizone. Accordingly, on the absorption curves of substituted 1,5-diphenylthiocarbazone, the maxima in the short-wave region belong to the thiol forms, and the maxima in the long-wave region to the thione forms.

From the equations $d_{\lambda\max_1} = lc_1\varepsilon_1$ and $d_{\lambda\max_2} = lc_2\varepsilon_2$ it follows that the ratio

$$\frac{d_{\lambda\max_2}}{d_{\lambda\max_1}} = \frac{c_2\varepsilon_2}{c_1\varepsilon_1},$$

whence the constant of tautomeric equilibrium is

$$K_{\mathrm{T}} = \frac{c_2}{c_1} = \frac{d_{\lambda\max_2}}{d_{\lambda\max_1}}\frac{\varepsilon_1}{\varepsilon_2}$$

$$pK_{\mathrm{T}} = \lg\frac{d_{\lambda\max_2}}{d_{\lambda\max_1}} + \lg\frac{\varepsilon_1}{\varepsilon_2}; \qquad (2)$$

where $d_{\lambda\max_2}$ and $d_{\lambda\max_1}$ are the optical densities (extinctions), c is the concentration, ε_1 and ε_2 are the molar extinction coefficients of the thiol and, respectively, thione, and l is the layer thickness.

As the experimental data show, the tautomeric equilibrium constant of dithizone and its substituted derivatives in solvents is approximately equal to the ratio $\frac{d_{\lambda\max_2}}{d_{\lambda\max_1}}$. The ratio $\frac{\varepsilon_1}{\varepsilon_2}$ is practically independent of the solvent.

Table 1

Thiocarbazone	Benzene $\varepsilon_1 \cdot 10^{-4}$	Benzene $\varepsilon_2 \cdot 10^{-4}$	Benzene $\varepsilon_1/\varepsilon_2$	Carbon tetrachloride $\varepsilon_1 \cdot 10^{-4}$	Carbon tetrachloride $\varepsilon_2 \cdot 10^{-4}$	Carbon tetrachloride $\varepsilon_1/\varepsilon_2$	Chloroform $\varepsilon_1 \cdot 10^{-4}$	Chloroform $\varepsilon_2 \cdot 10^{-4}$	Chloroform $\varepsilon_1/\varepsilon_2$	Hexane $\varepsilon_1 \cdot 10^{-4}$	Hexane $\varepsilon_2 \cdot 10^{-4}$	Hexane $\varepsilon_1/\varepsilon_2$
Diphenylthiocarbazone structure, C=S, with N=N and NHNH groups	11.92	11.93	1.0	12.0	11.9	1.0	12.2	12.7	0.96	8.6	8.6	1.0
o,o'-dimethyl derivative, CH_3 substituents, C=S, with N=N and NHNH groups	23.33	22.6	1.03	20.8	20.6	1.01	28.8	28.8	1.0	13.56	13.76	0.99
o,o'-ethoxy derivative, OC_6H_5 substituents, C=S, with N=N and NHNH groups	22.8	23.2	0.98	21.58	21.74	0.99	27.6	27.3	1.01	11.0	10.8	1.02

Table 2

No.	R	Source	Benzene a	Benzene b	Benzene K_T	Carbon tetrachloride a	Carbon tetrachloride b	Carbon tetrachloride K_T	Chloroform a	Chloroform b	Chloroform K_T	Hexane a	Hexane b	Hexane K_T
1	Phenyl	(13)	$\frac{450}{1.6}$	$\frac{620}{2.8}$	1.75	$\frac{450}{1.80}$	$\frac{620}{2.81}$	1.56	$\frac{450}{1.52}$	$\frac{610}{3.85}$	2.53	$\frac{450}{2.8}$	$\frac{620}{2.86}$	1.02
2	*o*-CH_3-phenyl	(14)	$\frac{470}{0.59}$	$\frac{630}{1.51}$	2.56	$\frac{470}{1.2}$	$\frac{630}{2.7}$	2.25	$\frac{450}{1.24}$	$\frac{620}{4.34}$	3.5	$\frac{450}{0.552}$	$\frac{630}{0.888}$	1.61
3	*o*-OC_6H_5-phenyl	(13)	$\frac{480}{1.0}$	$\frac{650}{2.34}$	2.34	$\frac{470}{1.056}$	$\frac{640}{2.1}$	1.99	–	–	–	$\frac{470}{0.54}$	$\frac{650}{0.79}$	1.46
4	*o*-OCH_3-phenyl	(13)	$\frac{486}{1.02}$	$\frac{659}{2.38}$	2.33	$\frac{470}{1.06}$	$\frac{640}{2.6}$	2.45	$\frac{470}{1.14}$	$\frac{620}{3.35}$	2.94	$\frac{440}{0.32}$	$\frac{630}{0.44}$	1.38
5	Dibromophenyl, Br substituents	(17)	$\frac{445}{1.30}$	$\frac{645}{1.29}$	0.99	$\frac{450}{0.678}$	$\frac{640}{0.55}$	0.81	$\frac{450}{0.536}$	$\frac{630}{0.745}$	1.39	$\frac{440}{1.23}$	$\frac{630}{0.725}$	0.59

Note. a: above the line $\lambda_{\max_1}$, below the line $d_{\lambda \max_1}$; b: above the line $\lambda_{\max_2}$, below the line $d_{\lambda \max_2}$.

solvent and is approximately equal to unity and, consequently, the value of the second term of equation (2) may be neglected.

For the calculation of the molar extinction coefficients ε_1 we took as 100% for the thiol form of the thiocarbazones the absorption intensity at the maxima of the corresponding S-methyl derivatives of dithizone, synthesized by us ([16]), of the general formula

RN=N
C(SCH₃)
RNHN

ε_2 was calculated by the formula:

$$\varepsilon_2 = \frac{d_{\lambda\ \max_2}}{l(a - a_1)},$$

where a is the weighed amount of the corresponding thiocarbazone in g-mol/l, and a_1 is the weight fraction of the thiol form in the weighed amount (a).

Fig. 1. Relationship between pK_{TS_2} and pK_{TS_1} for five thiocarbazones.
1 —1,5-di-(phenyl)-thiocarbazone, 2 —1,5-di-(o-tolyl)-thiocarbazone, 3 —1,5-di-(o-phenoxyphenyl)-thiocarbazone, 4 —1,5-di-(o-methoxyphenyl)-thiocarbazone, 5 —1,5-di-(2,4-dibromophenyl)-thiocarbazone.
I —S_1=benzene, S_2=hexane; *II* —S_1=carbon tetrachloride, S_2=hexane; *III* —S_1=carbon tetrachloride, S_2=benzene; *IV* —S_1=benzene, S_2=chloroform.

Table 1 gives the data for determining the constants of tautomeric equilibrium of three thiocarbazones in different solvents. In Table 2, for the thiocarbazones studied,

RN=N
\
C=S
/
RNHNH

the absorption maxima $\lambda_{\max_1}$ and $\lambda_{\max_2}$, the corresponding optical densities $d_{\lambda\,\max_1}$, $d_{\lambda\,\max_2}$, and their ratio

$$\frac{d_{\lambda\,\max_2}}{d_{\lambda\,\max_1}} = K_T$$

are presented.

As can be seen from the data of Table 2 and Fig. 1, the linear character of the dependence and the angle of inclination of the straight lines of 45° are maintained quite satisfactorily.

It may therefore be considered that the relation derived by M. I. Kabachnik, which extends the regularities of acid–base protolytic equilibrium to tautomeric keto–enol equilibrium, is confirmed in the series of arylthiocarbazones for thione–thiol tautomeric equilibrium.

Arylthiocarbazones (preparations Nos. 1–4) were synthesized by the formazyl method according to literature data ([14,15]). The absorption spectra of the thiocarbazones and their S-methyl derivatives were measured in the appropriate solvents at a concentration of $6.6 \cdot 10^{-5}$ g-mol/l on an SF-4 spectrophotometer.

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CITED LITERATURE

[1] M. I. Kabachnik, DAN, **83**, 407 (1952).
[2] M. I. Kabachnik, DAN, **83**, 859 (1952).
[3] M. I. Kabachnik, Izv. AN SSSR, OKhN, 1955, 98.

[4] M. I. Kabachnik, T. A. Mastryukova, Izv. AN SSSR OKhN, 1953, 163.
[5] M. I. Kabachnik, S. T. Ioffe, DAN, **91**, 833 (1953).
[6] M. I. Kabachnik, S. T. Ioffe, T. A. Mastryukova, ZhOKh, No. 2 (1955).
[7] M. I. Kabachnik, Usp. khim., **25**, 137 (1956).
[8] A. N. Nesmeyanov, M. I. Kabachnik, in: *Problems of Chemical Kinetics, Catalysis, and Reactivity*, Publishing House of the Academy of Sciences of the USSR, 1955, pp. 644–698.
[9] A. N. Nesmeyanov, M. I. Kabachnik, ZhOKh, **25**, 41 (1955).
[10] M. I. Kabachnik, in: *Problems of the Mechanism of Organic Reactions*, Kiev, 1954, pp. 126–156.
[11] J. N. Brönsted, Z. phys. Chem., A, **169**, 32 (1934).
[12] N. A. Izmailov, ZhFKh, **24**, 321 (1950).
[13] P. S. Pel' kis, DAN, **88**, 999 (1953).
[14] D. S. Tarbell et al., J. Am. Chem. Soc., **70**, 1385 (1948).
[15] P. S. Pel' kis, L. S. Pupko, Ukr. khim. zhurn., **17**, 93 (1951).
[16] P. S. Pel' kis, R. G. Dubenko, DAN, **110**, 798 (1956). P. S. Pel' kis, R. G. Dubenko, L. S. Pupko, ZhOKh, **27**, 2134 (1957).

Note: Figure translations are in progress. See original paper for figures.