Chemistry

Academician A. E. Arbuzov and Yu. P. Kitaev

1957

SovietRxiv

Abstract

Full Text

Chemistry

Academician A. E. Arbuzov and Yu. P. Kitaev

STUDY OF THE TAUTOMERISM AND GEOMETRICAL ISOMERISM OF CERTAIN ARYLHYDRAZONES BY THE POLAROGRAPHIC METHOD

It is known that, when dissolved in alcohol, phenylhydrazones are partially converted into aliphatic-aromatic azo compounds [1,2]. Suggestions have been made concerning the possible existence of yet another tautomeric form, constructed according to the ene-hydrazine type [3–5]; however, its existence has not yet been proved.

There is an extensive literature on the stereoisomerism of arylhydrazones; many compounds of this class have been isolated in two forms [6,7]. Attempts to obtain different derivatives from both isomers have not been successful [7,8], and the appearance of two forms, by analogy with the isomerism of oximes, has customarily been regarded as geometrical isomerism. But N. V. Khromov-Borisov [9] recently showed that there can be no complete analogy between the stereoisomerism of oximes and that of hydrazones. Recently, the stereoisomerism of colored nitrophenylhydrazones has been intensively studied by the spectral method [10–12].

Thus, the tautomerism and stereoisomerism of arylhydrazones have still been studied quite insufficiently.

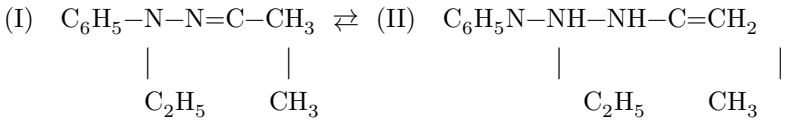
Since it is known that tautomeric forms and stereoisomers are reduced at a mercury dropping electrode at different potentials, in the present work the polarographic method was chosen; with its aid the changes occurring when arylhydrazones are dissolved in alcohol were monitored.

Polarograms were recorded during storage in the dark of methanolic solutions of the phenylhydrazones of acetone, methyl ethyl ketone, methyl isopropyl ketone, cyclohexanone, acetophenone, *n*-chloroacetophenone, acetic and benzoic aldehydes. A borate buffer with pH = 7.2 served as the supporting medium; the concentration of the solutions studied was $\sim 0.6–1.2 \cdot 10^{-2}$ mol.; the polarograms were recorded at 20° on a visual polarograph of the M8-2000 type. The half-wave potentials ($\varepsilon_{1/2}$) were determined graphically and referred to the saturated calomel electrode. For each solution, families of polarograms were obtained, characterizing the changes that occurred in the solutions over a definite

time. In the changes of the curves, regularities were found: on the polarograms of the phenylhydrazones of aliphatic ketones and of cyclohexanone, the initial waves with $\varepsilon_{1/2}$ about −1.40 V disappeared with time; waves with $\varepsilon_{1/2} \sim -0.7$ V appeared and grew; and waves with $\varepsilon_{1/2} \sim -1.08$ V appeared, grew, and then decreased. The latter waves usually each split into two new ones, one of which —with the less negative potential—gradually disappeared. The initial waves of solutions of the phenylhydrazones of aldehydes and aliphatic-aromatic ketones were located at potentials less negative than −1.4 V.

The interpretation of the polarograms obtained was carried out as follows. Additional polarograms were recorded of solutions in methanol of azobenzene, as a model of the azo form, and of ethyl phenylhydrazone of acetone, as a compound incapable of forming an azo form. Under our conditions azobenzene was reduced at −0.5 V, i.e., the waves of the azo forms of arylhydrazones should

be located near this potential. Winkel and Siebert ([13]), using polarography, showed that under the action of light azobenzene in alcoholic solution passes into a labile syn form, which in the dark rearranges into the stable anti isomer. Consequently, the appearance that we observed of waves at potentials −0.68, −0.75 V, their separation into two waves with $\varepsilon_{1/2}$ −0.56, −0.76 V and −0.84, −0.97 V, and the subsequent growth of the latter on the polarograms of the phenylhydrazones studied corresponded to the formation of a mixture of stereoisomers of the azo form and to the gradual disappearance in the dark of the labile syn isomer. On the polarograms of ethylphenylhydrazone of acetone there were only two waves at potentials −1.20 and −1.50 V, which corresponded to the two tautomers possible for it, (I) and (II):



The phenylhydrazone of benzaldehyde cannot form an enehydrazine and, apart from the wave belonging to the free aldehyde, the polarograms of its alcoholic solution contained two pairs of waves, one of which must be assigned to the syn and anti isomers of the azo form ($\varepsilon_{1/2} = -0.56$ and −0.89 V); consequently, the second pair belongs to the two isomers of the hydrazone form ($\varepsilon_{1/2} = -1.08$ and −1.20 V).

Thus it was found that potentials from −1.40 to −1.55 V correspond to the waves of enehydrazines, and from −1.0 to −1.30 V to the waves of hydrazones.

Deciphering the families of polarograms obtained by us showed that the phenylhydrazones of acetone, methylethyl ketone, methyl isopropyl ketone, cyclohexanone, and ethyl phenylhydrazone acetone, contrary to the generally accepted view, are not hydrazones—in the free state they are constructed according to the syn-enehydrazine type.

Table 1

Compounds	Azo form a	Azo form	Azo form	Azo form	Hydrazone form a	Hydrazone form	Hydrazone form	Hydrazone form	Enehydrazine form a	Enehydrazine form	Enehydrazine form
$PhNHN{=}C(CH_3)CO_2H$	0.66	0.84	0.73	15.4	1.08	–	–	18.0	1.45	–	–
$PhNHN{=}C(CH_3)COC_2H_5$	0.68	0.87	0.77	20.2	1.08	1.30	10.1	13.8	1.44	1.55	5.1
$PhNHN{=}C(CH_3)COCH(CH_3)_2$	0.72	0.84	0.81	16.6	1.00	1.19	8.7	15.6	1.44	–	–
$PhNHN{=}C(CH_3)C_6H_4OH$	0.76	0.97	0.9	19.8	–	1.30	–	9.2	–	1.50	–
$PhNHN{=}C(CH_3)COC_6H_5$	0.65	0.98	0.82	18.4	1.15	1.28	6.0	–	–	–	–
$PhNHN{=}C(CH_3)COC_6H_4Cl_p$	0.64	0.92	0.79	17.0	1.06	1.27	9.7	–	–	–	–
$PhNHN{=}C(CH_3)C_6H_5Cl_o$	0.56	0.89	0.72	18.9	1.08	1.20	5.5	–	–	–	–
$PhNHN{=}CHCH_3$	0.50	0.78	0.69	19.3	1.05	1.15	5.0	11.5	1.35	–	–
$PhNHNH_2 + (CH_3)_2CHCHO$	–	–	–	–	–	1.26	–	–	–	–	–

Note. *a* –everywhere $-\varepsilon_{1/2}$ of the syn isomers (V), –everywhere $-\varepsilon_{1/2}$ of the anti isomers (V), –everywhere the energy of transition syn → anti (kcal/mole), –everywhere the energy of transition hydrazone → azo compound (kcal/mole), –the energy of transition enehydrazine → hydrazone (kcal/mole).

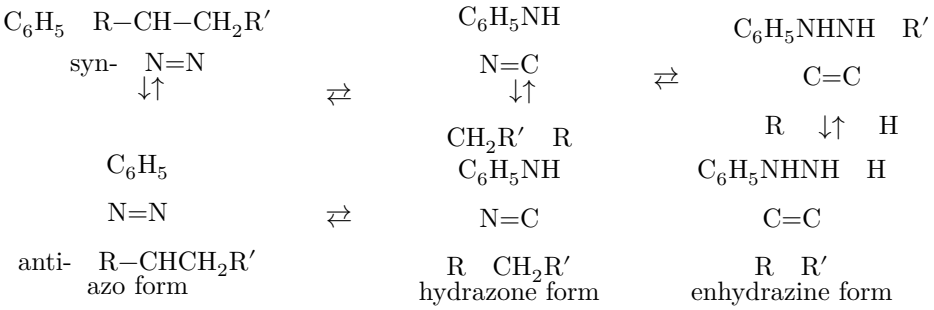
The phenylhydrazone of methylethyl ketone, on dissolution in alcohol and storage of the solution in the dark, also forms the anti isomer of the enehydrazine form. The phenylhydrazones of aldehydes, as well as those of acetophenone and *p*-chloroacetophenone, in the free state have the structure of anti hydrazones. Upon dissolution of all the compounds studied, with the exception of ethylphenylhydrazone of acetone, in alcohol, a tautomeric transformation of them into mixed azo compounds takes place according to the scheme:

enehydrazine → hydrazone → azo compound.

Table 1 gives the half-wave potentials of the tautomers and stereoisomers that we found, and the energies of their mutual transitions, calculated from the difference of the potentials by the method of Winkel and Siebert ([13]).

The polarographic study of a series of phenylhydrazones showed that in the general case they can exist in three tautomeric forms, each

of which possesses stereoisomerism:



The ability of the tautomeric forms to be reduced indicates the presence in their molecules of conjugated bonds, since it is known that isolated multiple bonds either are not reduced at all under these conditions or are reduced only at considerably more negative potentials.

The different structures of arylhydrazones of aldehydes and fatty-aromatic ketones, on the one hand, and of aliphatic and alicyclic ketones, on the other, can be explained as follows. The interaction of an arylhydrazine with a carbonyl compound proceeds in two stages [14]. At first addition takes place at the double carbonyl bond:

$$\mathrm{ArNHNH{-}H + O{=}C(R){-}R' \rightarrow ArNHNH{-}C(H)(R){-}R'} \qquad (1)$$

The further transformation of this intermediate carbinol depends on the structure of the initial carbonyl compound. Thus, if an aldehyde was taken, a carbinol is formed in which the action of the free electron pair of the nitrogen atom that is conjugated with the bonds of the aromatic ring on the free electron pair of the second nitrogen atom is stronger than the action on them of the electrons of the oxygen atom. Owing to πPP-conjugation, the $N—H$ bonds are weakened, and one of them enters into conjugation with the polar $C—O$ bond.

It is known [15] that the condition for the greatest conjugation is parallelism, i.e., a trans arrangement of the bonds. Therefore free rotation about the bond of nitrogen with the aliphatic carbon in the carbinol is hindered, and the most energetically favorable structure is structure (III).

The polarity of the carbinol molecules will cause their orientation and mutual approach, and, on approaching, the molecules will interact through the terminal atoms of the $\sigma\sigma$-conjugated system. Redistribution of the electrons in the systems leads to the formation of water and the anti-isomer of the hydrazone:

$$\begin{gathered}\text{(III)}\quad \mathrm{Ar{-}\ddot{N}{-}H \cdots N{-}C(H)(R){-}OH} \\ \text{and the associated carbinol molecules} \\ \longrightarrow \mathrm{ArNH{-}N{=}C(H)(R) + H_2O}\end{gathered} \qquad (2)$$

The presence of a second alkyl group at the carbon atom in the intermediate carbinol from a ketone introduces changes into the interaction of the bonds: under its influence the polarization of the C—O bond is intensified and its interaction is weakened—

with the N—H bond, but conditions are created that favor conjugation with the C—H bond of the neighboring carbon atom. This makes structure IV the most energetically favorable, in which free rotation about the

$$\overset{1}{\mathrm{C}}-\overset{2}{\mathrm{C}}$$

bond is hindered.

$$\text{(IV)}\quad \mathrm{Ar{-}NH\cdots N(H){-}C(R)(OH){-}C(H)(R')} \longrightarrow \mathrm{Ar{-}NH{-}N(H){-}C(R){=}C(H)R'}\quad \text{(V)}$$

The subsequent intermolecular elimination of water, proceeding according to a scheme analogous to (2), gives the syn-isomer of the enhydrazine (V). Alicyclic ketones react in the same way; but if R = Ar, then the second stage of the interaction of an arylhydrazine with a fatty-aromatic ketone proceeds according to the aldehyde type. The fact that the reaction proceeds stepwise is supported by the observation that, when an arylhydrazine and a carbonyl compound are mixed, heating is first observed without disruption of homogeneity, and only after some time does instantaneous turbidity occur and water separate. The latter circumstance indicates a chain mechanism for the second stage.

It has long been known that the phenylhydrazone of acetaldehyde can be prepared in two forms, which are customarily regarded as stereoisomers. It has been found that, when these isomers are dissolved in most solvents, their mutual transformation occurs, with preferential formation of the higher-melting form ([7]).

Using polarography, we found that these forms of acetaldehyde phenylhydrazone are not stereoisomers but tautomers, namely: the substance with m.p. 57°, obtained by the interaction of the components in ether in the cold or from the second form by treatment with an alcoholic solution of SO_2, is the anti-isomer of phenylhydrazone ($\varepsilon_{1/2}$ = 1.16 V, in dioxane), whereas the substance with m.p. 98—101° proved to be 2-phenylhydrazinoethylene ($\varepsilon_{1/2} = -1.35$ V).

We were further able, by the method of Thiele and Pickard ([16]), to obtain two isomers of benzaldehyde phenylhydrazone and to show that the isomer with m.p. 134—6° is the syn-form ($\varepsilon_{1/2} = -1.06$ V), and the isomer with m.p. 152° is the anti-form ($\varepsilon_{1/2} = -1.16$ V) of the hydrazone. Studies of the tautomerism and stereoisomerism of arylhydrazones are continuing.

Chemical Institute named after A. E. Arbuzov
Kazan Branch of the Academy of Sciences of the USSR

Received
12 XI 1956

CITED LITERATURE

1. E. Ch. C. Baly, W. B. Tuck, *J. Chem. Soc.*, **89**, 982 (1906).
2. M. P. Grammaticakis, *C. R.*, **206**, 1307 (1938).
3. P. C. Freer, *Lieb. Ann.*, **283**, 391 (1894).
4. G. M. Robinson, R. Robinson, *J. Chem. Soc.*, **113**, 639 (1918).
5. K. Auwers, H. Winderling, *Ber.*, **64**, 2748 (1931).
6. Zd. H. Skraup, *Monatsh.*, **10**, 401 (1889).
7. G. Lockemann, O. Liesche, *Lieb. Ann.*, **342**, 14 (1905).
8. B. Overton, *Ber.*, **26**, 21 (1893).
9. N. V. Khromov-Borisov, *ZhOKh*, **25**, 136 (1955).
10. W. Theilacker, *Ber.*, **82**, 190 (1949).
11. F. Ramirez, A. F. Kirby, *J. Am. Chem. Soc.*, **76**, 1037 (1954).
12. F. Bohlmann, *Ber.*, **84**, 490 (1951).
13. A. Winkel, H. Sibert, *Ber.*, **74**, 670 (1941).
14. M. J. S. Dewar, *The Electronic Theory of Organic Chemistry*, Oxford, 1949, p. 115.
15. A. N. Nesmeyanov, *Uch. zap. MGU*, issue 132, 5 (1950).
16. J. Thile, R. H. Pickard, *Ber.*, **31**, 1249 (1898).

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