CHEMISTRY

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1960

SovietRxiv

Abstract

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CHEMISTRY

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ON THE STRUCTURE OF CERTAIN CYCLIC 2-NITRODIKETONES-1,3

Continuing the studies begun by us on the tautomerism of cyclic 2-nitrodiketones-1,3 ([1,2]), we have investigated 2-nitrodimedone (I, $R_1 = R_2 = CH_3$), 2-nitro-5-phenylcyclohexanedione-1,3 (2-nitrophenedione; I, $R_1 = H$, $R_2 = C_6H_5$) and their anions, as well as certain related compounds. In the course of the investigations the structure of these compounds was elucidated, as was also the distinction among three nitration products of phenedione: the compound with m.p. 120-121°, obtained on crystallization from benzene; the compound with m.p. 131-132°, obtained on precipitation from saturated aqueous solutions with hydrochloric acid ([3]); and the compound with m.p. 119-120°, obtained on crystallization from aqueous solutions, but corresponding in elemental composition to a product with one molecule of water.

IR spectra were taken for the substances in the solid state (suspensions in paraffin oil) and in chloroform solutions; ultraviolet spectra were taken for 10^{-4} M solutions of the compounds in H_2O, CH_3OH, or $CHCl_3$. Polarograms were recorded for 10^{-4} M aqueous solutions of the substance in Britton-Robinson buffer solutions against a background of 0.1 N KCl. A summary of the experimental data is presented in Table 1. From the IR spectra it follows that 2-nitrodimedone and 2-nitrophenedione in chloroform have the same structure, namely the nitroenol form, in which the hydroxyl group has entered into a strong intramolecular hydrogen bond.

(I) (II) (III) (IV)

From the individual absorption frequencies, the frequency at $\sim$ 1540 cm^{-1} should be assigned to vibrations of the nitro group, the frequency at $\sim$ 1570 cm^{-1} to vibrations of the $C{-}C$ bond, lowered in comparison with the enol ether of dimedone, and the frequency at 1690 cm^{-1} to vibrations of the carbonyl group, raised in comparison with vibrations of a normally conjugated carbonyl. The latter is explained by some change in the bond order of the $C = C$ bond as a consequence of formation of a strong intramolecular ring, which is the reason for the decrease in the effect of conjugation of the carbonyl and the double bond.

The identical structure of the molecules of 2-nitrodimedone and 2-nitrophenedione in chloroform solutions is also confirmed by the similarity of the corresponding ultraviolet absorption spectra: both compounds in the interval 2370-3500 Å have an absorption band at 2930 (2960) Å, caused by the chromophoric grouping $OH-\overset{|}{C}=\overset{|}{C}-NO_2$; an absorption maximum of the grouping $>C=\overset{|}{C}-\overset{|}{C}=O$ is not observed because of the strong absorption of chloroform. In the case of 2-nitrodimedone, the IR spectrum of the solid substance

noticeably different from the spectrum in chloroform solution. It follows from the spectrum that 2-nitrodimedone in the solid state also exists in the nitroenol form, but in this case it is not intramolecular but intermolecular interaction of the groups that predominates.

By contrast, the IR spectra of solid 2-nitrophendione show, first, that two modifications with different melting points (131-132° and 120-121°) have one and the same structure and, second, that the structure

Table 1

Compound	IR absorption in cm^{-1} (in parentheses—percent absorption), solid substance	IR absorption in cm^{-1} (in parentheses—percent absorption), $CHCl_3$	UV absorption in Å (in parentheses—values of $\varepsilon \cdot 10^4$), H_2O	UV absorption in Å (in parentheses—values of $\varepsilon \cdot 10^4$), CH_3OH	UV absorption in Å (in parentheses—values of $\varepsilon \cdot 10^4$), $CHCl_3$	Polarographic half-wave equation $E_{1/2}$, V
2-Nitrodimedone	1523 (100);1625 (94);1661 (83)	1547 (93);1564 (95);1690 (88)	2620 (1.50)*;3330 (1.31)	–	2960 (0.70)	
2-Nitrophenedione (m.p. 131-132°)	1525 (84);1559 (93);1682 (88)	1542 (89);1567 (96);1689 (88)	–	–	2930 (0.53)	
2-Nitrophenedione (m.p. 120-121°)	1523 (88);1556 (97);1682 (88)	–	2610 (1.46);3330 (0.34)	–	–	

Compound	IR absorption in cm^{-1} (in parentheses—percent absorption), solid substance	IR absorption in cm^{-1} (in parentheses—percent absorption), $CHCl_3$	UV absorption in Å (in parentheses—values of $\varepsilon \cdot 10^4$), H_2O	UV absorption in Å (in parentheses—values of $\varepsilon \cdot 10^4$), CH_3OH	UV absorption in Å (in parentheses—values of $\varepsilon \cdot 10^4$), $CHCl_3$	Polarographic half-wave equation $E_{1/2}$, V
NH_4 salt of 2-nitrodimedone (m.p. 190–192°)	1568 (90);1625 (68)	–	–	2650 (1.73)	–	−1.16-0.080pH
NH_4 salt of 2-nitrophendione (m.p. 197–198°)	1577 (96);1612 (infl.)	–	–	2640 (1.69)	–	−0.11-0.066pH
2-Nitro-2-methyldimedone	1560 (98);1715 (97);1748 (82)	–	–	–	–	–
2,2-Dimethyldimedone	1694 (46);1724 (49)	1702; 1730 ([9])				
Ethyl ester of dimedone	1613 (93);1669 (89)	1605 (90);1645 (68) ([14])	–	2500 (1.92)	–	

6-Nitro-3-phenylhexan-5-one acid (m.p. 119-120°)	1560 (100);1696 (10);1728 (85)	–	2350 (infl.)**;3330 (0.39)2320 (0.29) in 1 *N*3280 (1.16) KOH	–	–	−0.12-0.074pH***−0.69-0.03pH	

* Potassium salt in aqueous solution ~ 2610 Å (1.52) and ~ 3400 Å (0.29) ([13]).
** On standing, ε decreases rapidly (within 24 hours to 0.11).
*** On standing, the wave decreases rapidly.

is close to the state of the molecule in $CHCl_3$ solution, i.e., it is a nitroenol with an intramolecular hydrogen bond, although intermolecular interaction may also occur to some extent. The known difference between 2-nitrophendione and 2-nitrodimedone in the solid state can apparently be explained by crystallochemical factors, and also by hindrance of the intermolecular interaction in 2-nitrophendione due to the presence of a sterically encumbering phenyl radical. In both investigated compounds, in the region 2400-4000 cm^{-1}, apart from vibrations of the C—H bond, nothing could be detected; possibly the C—H and O—H vibrations overlap.

The third "modification"of 2-nitrophendione, with m.p. 119-120°, has an entirely different structure; at first it seemed to us to be identical with the modification of m.p. 120-121°. However, the strong depression of the melting point on mixing, the presence of an additional water molecule in the composition of the molecule, the absence of color in alkaline solutions, and the spectroscopic and polarographic data convinced us that the formation of the "hydrate" is associated with opening of the six-membered ring and that the substance is 6-nitro-3-phenylhexan-5-one acid (IV). This is proved by its IR spectrum, where the frequency at 1560 cm^{-1} corresponds to the enhanced oscilla-

vibrations of the nitro group (as a result of the influence of the neighboring carbonyl), the frequency at 1695 cm^{-1} to the carboxyl group, and the frequency at 1728 cm^{-1} to carbonyl vibrations increased as a result of the influence of the nitro group. Compound (IV), as an α-nitro ketone, rapidly decomposes in aqueous solutions ([4]) into nitromethane and β-phenylglutaric acid, as is proved by the UV spectra and polarograms of the solutions. On storage of the solution, the maximum at 3300 Å rapidly decreases and, after a week, all absorption in the near ultraviolet disappears. Freshly prepared solutions of the substance give a polarographic wave with $E_{1/2} = -0.49$ V (pH 5), which rapidly decreases owing to the appearance of a new wave with $E_{1/2} = -0.84$ V (pH 5); the latter may be assigned to nitromethane ([5]). Consequently, on boiling in aqueous solutions, 2-nitrophendione opens the ring comparatively easily, with formation

of 6-nitro-3-phenylhexan-5-oic acid, which is unstable in aqueous solutions.

The IR spectra of solid ammonium salts of 2-nitrodimedone and 2-nitrophendione indicate the existence of the mesomeric anion (II), where the charge distribution takes place between two carbonyls and the nitro group. The fractions of the charges δ, δ', and δ'', localized at the individual centers, are still difficult to estimate, but it may be assumed that in these systems the electron density on the carbonyl groups is greatly reduced, as evidenced by the hypsochromic shift of the K band in the UV spectra in comparison with the unsubstituted enolate anion ([6]), and by the shift of the characteristic frequencies of the enolate anion (1500–1520 cm^{-1}) ([7]) toward higher frequencies in the IR spectra. At the same time, comparing the shifts of the maxima of the IR and UV absorption spectra of the anions of cyclohexanediones-1,3 and their nitro derivatives, on the one hand, and of indandione-1,3 ([8]) and 2-nitroindandione-1,3 (maxima of UV absorption in aqueous solutions 2270 Å (1.83), 2410 (1.56-infl.), 3030 (1.16), and 3470 (1.87)), on the other, it seems probable that the distribution of electron density in mesomeric 2-nitroenolate anions is different; namely, in the case of the anions of 2-nitrocyclohexanediones-1,3 the distribution corresponds to a greater degree to the enolate anion, and not to the aci-nitro form, as is the case with 2-nitroindandione-1,3 ([2]).

As a model substance for the nitrodiketo form, 2-nitro-2-methyldimedone (III) was chosen; here the frequency at 1560 cm^{-1} is assigned to vibrations of the nitro group, and the frequencies at 1715 and 1750 cm^{-1} to vibrations of the carbonyl groups. Comparison of 2-nitro-2-methyldimedone with 2,2-dimethyldimedone shows that the frequencies of the carbonyl groups in α-nitro ketones are increased in comparison with the normal carbonyl frequency; in turn, the frequencies of the nitro group here are also increased (from 1540 to 1560 cm^{-1}). A similar influence of the interaction of the nitro group with the α-carbonyl on the IR spectra is also revealed from some literature data ([9],[10]).

Comparison of 2-nitrodimedone and 2-nitrophendione with 2-nitroindandione-1,3 ([2]) leads to the conclusion that these compounds differ fundamentally in structure. If the first two in the solid state are nitroenols, then the latter exists in the form of a nitrodiketone or an ionized nitronic acid. If the anions of the salts of 2-nitrodimedone and 2-nitrophendione are apparently closer to the structure of the enolate anion, then the anion of 2-nitroindandione-1,3 almost completely corresponds to the structure of the anion of the aci-nitro form. Potentiometric measurements show that 2-nitrodimedone and 2-nitrophendione in aqueous solutions are acids with dissociation constants of the order of 10^{-3}, i.e., in strength approximately equal to formic acid, whereas 2-nitroindandione-1,3 is a strong acid, completely dissociated at all concentrations.

A certain confirmation of the structural difference between the anions of 2-nitrodimedone (2-nitrophendione) and 2-nitroindandione-1,3 is also provided by their polarographic behavior; namely, the "nitro group" in the first two anions is reduced somewhat more readily than the "nitro group" in 2-nitroindandionate,

despite conjugation with the aromatic nucleus in the molecule

of the latter, which accounts for the considerably easier reducibility of the carbonyl in 2-nitroindan-1,3-dionate as compared with 2-nitrodimedonate and 2-nitrophenedionate ([11]).

The structural differences set forth above can be explained if one takes into account that 2-nitrodimedone and 2-nitrophenedione have a stable six-membered ring, whereas the molecule of 2-nitroindandione-1,3 contains a more strained five-membered ring, in which endocyclic double bonds are less favorable than exocyclic ones ([2]). Therefore, in the case of 2-nitroindandione-1,3 there is a tendency toward formation of the ketonitronic acid form, whereas in the case of alicyclic six-membered nitro-β-diketones formation of the nitroenol is possible.

The UV spectra were recorded by A. Grinvalde and M. Tiltin.

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Received
23 XI 1959

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