REACTIONS OF N-VINYL INDOLE WITH HYDROGEN HALIDES

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Khimiya Geterotsiklicheskikh Soedinenii, Vol. 4, No. 6, pp. 1025–1028, 1968

UDC 547.751.542.944.5

N-vinyl indole was brought into reaction with hydrogen chloride, hydrogen bromide, and hydrogen iodide. It was shown that, by reacting with the pyrrole rings of polyvinyl indole, hydrogen halides form complex compounds, with simultaneous charge transfers.

Hydrogen chloride and bromide are easily added to simple vinyl esters at the double bond, thus forming α-halogen esters [1].

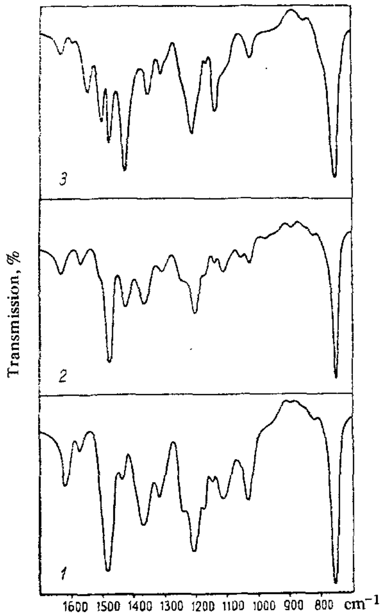


Fig. 1. IR spectra of polyvinyl indole (1) of the HBr addition product of N-vinyl indole (2), and of the HCl addition product of N-vinyl indole (3).

By substituting in the vinyl compound the oxygen atom by nitrogen, this reaction follows a peculiar course, evidently due to the lower electronegativity of the nitrogen atom with its single pair of unshared electrons. Thus, it is known that the addition of hydrogen halides to vinyl lactams follows a more complex course. The reaction of vinyl pyrrolidone with hydrogen chloride, taken in equimolecular quantities, gives rise to a series of unstable reaction products [2]. Efforts to establish the structure of these products either chemically or spectroscopically have not proved successful. It was not possible to separate either the α- or the β-halogen derivatives. It is also known that small amounts of HCl provoke the dimerization of vinyl pyrrolidone [3].

Until recently, there was no literature reference on the reactions of N-vinyl indole with hydrogen halides. It was, therefore, interesting to investigate the action of hydrogen chloride, hydrogen bromide, and hydrogen iodide on this compound. Our research established that N-vinyl indole vigorously reacts with hydrogen halides in the cold, in a CCl_4 medium. High yields of intensively colored and stable on storage compounds were obtained. Table 1 presents the properties of some of them.

It should be noted that the share of halogen atoms in the compounds formed depends on the ratio between the original reactants. When the hydrogen halide and N-vinyl indole are taken in equimolecular ratio, red, cherry-red, and brownish powders are obtained. These products contain about 9–11% chlorine, 25–30% bromine, and 10% iodine. They melt at from 120° to 170° C, and dissolve with difficulty in water and in organic solvents. When an excess of HCl or HBr is present, the chlorine and bromine content of the reaction products increase to 20 and 35%, respectively. The molecular weights of these compounds are in the order of magnitude of 900-1400. When this is correlated with the data on empirical formula determinations, the molecular weights correspond mainly to tetra- and pentameric halogen derivatives of vinyl indole. All the products of the hydrogen halide treatment of vinyl indole are stable to the hydrolytic action of acids and alkalies in aqueous medium. Their properties are not altered after a 25 hr boiling in dilute H_2SO_4 or in caustic alkali.

Table 1

Results of Treating N-Vinyl Indole (VIN) (in CCl_4 at 15° C) With Hydrogen Halides

Reaction conditions		Properties of the reaction products				Yield, %
ratio between the reactants	time, min	mp, °C	empirical formula	halogen, %		
				found	calculated	
VIN : HCl, 1 : 1	80	134—148	$C_{50}H_{45}N_5 \cdot 2HCl$	9.13	9.01	89
Excess HCl	45	122—124	$C_{60}H_{54}N_6 \cdot 6HCl$	19.55	19.67	82
VIN : HBr, 1 : 1	90	146—168	$C_{50}H_{45}N_5 \cdot 3HBr$	25.18	25.05	83
Excess HBr	150	220—226	$C_{40}H_{36}N_4 \cdot 4HBr$	35.53	35.71	99
VIN : HI, 1 : 1	130	131—140	$C_{80}H_{72}N_8 \cdot HI$	9.81	9.98	99

It is interesting that catalytic quantities of dry HCl or HBr induce the low molecular polymerization, up to the 8-th or 10-th stage, of N-vinyl indole. The substances thus formed contain practically no halogen, and are colorless powders readily soluble in acetone.

Our investigations showed that the addition of hydrogen halides to N-vinyl indole, a reaction apparently simple and smooth going, is in reality a very complex process. It is natural to suppose that in this case several concurrent reactions take place.

It is known that, under the action of HCl on indole, there is a dimerization of the latter at the third position in the five-member cycle, with addition of HCl to the nitrogen [4]. We showed that, under the conditions of the reaction here studied, indole and N-ethyl indole are indeed dimerized, with the formation of the corresponding hydrochlorides of indole and diethyl indole. In this connection it becomes evident that, in the case of N-vinyl indole, the addition of HCl is possible not only at the double bond of the vinyl group but also at the nitrogen atom. Nevertheless, the dimerization of N-vinyl indole at position 3 in the pyrrole cycles is not very likely, since it is known that the presence of a vinyl group stabilizes the heterocycles in question with respect to polymerization [5]. Calculations of the density distribution of π-electrons in the molecules of indole and of N-vinyl indole with the help of the semiempirical modification of the SSP MO LCAO method also leads to the conclusion that position 3 in N-vinyl indole is relatively inactive to the effect of electrophilic reagents (Table 2).

Furthermore, as previously stated, under the influence of catalytic quantities of hydrogen halides, the double bond of the vinyl group is easily activated, with the formation of polyvinyl indole. It may be supposed that, even when the reactants are in other ratios, vinyl polymerization plays the dominating role.

With the purpose of determining the structure of the products of the reaction between hydrogen halides and N-vinyl indole, we performed several physicochemical analyses. A joint examination of the IR-spectra in the 700–1700 cm^{-1} region of polyvinyl indole and of the products of the reactions of N-vinyl indole with HCl and HBr showed that, taking into account the variation in the intensity of isolated lines, the vibration spectra of these compounds are sufficiently similar (Fig. 1). They exhibit a series of bands characteristic of the vibrations of the indole ring (~1610, 1560, 1230–1200, 1020 cm^{-1}); and, most important, a line with a frequency at about 740 cm^{-1} which corresponds to its skeletal vibrations [6]. It is worth noting the absence in the IR-spectra of sufficiently intensive absorption in the 1380 cm^{-1} region, and this may be attributed to the symmetrical deformation vibrations of the bonds in the CH_3-groups. There is no appreciable absorption in the region of the valence vibrations of the double bond in the vinyl group. Thus, the hypothesis as to the polymerization of N-vinyl indole through the vinyl group under the influence of hydrogen halides is fully substantiated.

Table 2

π-Electron Charges in Indole and in N-Vinyl Indole

Position	Indole	N-Vinyl indole
1	+0.195	+0.239
2	−0.042	−0.047
3	−0.059	−0.052

The dark color of the reaction products and their high halogen content led us to believe that hydrogen halides are linked to the indole ring through a donor-acceptor bond, and this gives rise within the polymeric chain to complexes involving charge transfers. To follow the Mulliken's classification, such types of complexes should be referred to the π_n, σ type [7].

Some absorption bands in the 250–550 nm (nanometer) region were detected in the electronic absorption spectra (Fig. 2) of the reaction products with HCl and HBr when dissolved in dioxane. Indole, polyvinyl indole, and N-vinyl indole absorb in the 300 nm and in the far ultraviolet region. Therefore, absorption bands found at shorter wavelengths than 300 nm should be regarded mainly as absorption bands of the indole cycles. The presence of a broad band with a maximum

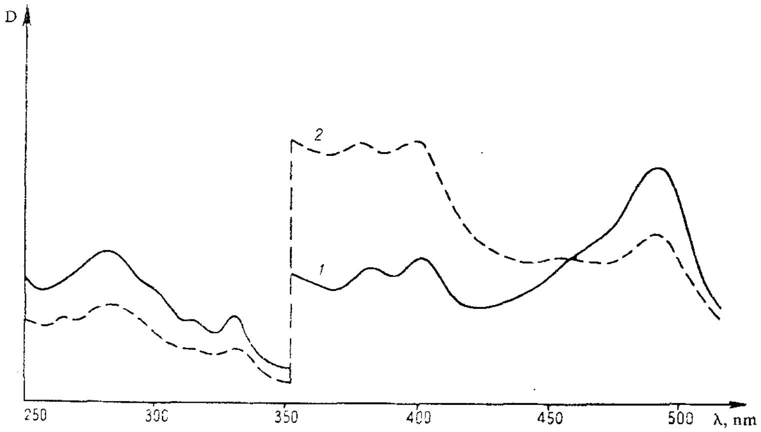
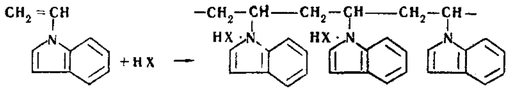


Fig. 2. UV spectra of the HBr (1) and of the HCl (2) addition products of N-Vinyl Indole.

at 490–500 nm and absorption in the 350–400 nm region are a result of complex formation with charge transfer between indole cycles and hydrogen halides molecules. A very decisive argument in support of this view is the presence of an EPR signal in all the reaction products of hydrogen halides with N-vinyl indole in contrast with the absence of such a signal in polyvinyl indole. The data at our disposal allow us to represent the structure of the reaction products of N-vinyl indole and hydrogen halides as a polymeric complex obtained according to the following scheme:



Depending on the reaction conditions, the hydrogen halide molecules may be linked to all the indole cycles of the polymeric chain or only to some of them.

EXPERIMENTAL

N-Vinyl indole was prepared by the reaction of acetylene and indole in the presence of alkali; bp 71° (1 mm), N^{20}_{D} 1.6330.

Addition of HCl to N-vinyl indole. To a solution of 0.46 g (0.013 mole) of HCl in 35 ml of CCl_4, 1.14 g (0.008 mole) of N-vinyl indole was added, under cooling, in the course of 10 min. Mixing of the reactants was continued at -15° C for another 2 hr. The red precipitate was filtered off, washed a few times with CCl_4, and dried under vacuum (2–3 mm) to constant weight. 1.08 g of N-vinyl indole hydrochloride was obtained, mp 129–134° C, Found, %: Cl 11.57; M (in camphor according to Rast) 620. Calculated for $C_{40}H_{36}N_4 \cdot 2HCl$, %: C 11.01; M 640.

Addition of HBr to N-vinyl indole. A current of HBr was passed through a solution of 2.1 g (0.015 mole) of N-vinyl indole in 30 ml CCl_4 at −15° C until a precipitate appeared. After 1 hr 30 min the cherry-colored precipitate was separated, washed with CCl_4, and dried under vacuum. 3.16 g of N-vinyl indole hydrobromide was obtained, mp 155–170° C. Found, %: Br 30.90; M 1012 (in camphor, according to Rast). Calculated for $C_{50}H_{45}N_5 \cdot 4HBr$, %: Br 30.79; M 1035.

A similar procedure was followed in the investigation of the reactions of N-vinyl indole with hydrogen halides taken in other ratios, as well as with hydrogen iodide. Table 1 presents the results obtained. The IR-spectra were recorded in a UR-10 spectrophotometer by pressing the material into KBr pellets (NaCl prism). The UV-spectra of the sample dissolved in dioxane were recorded in an SF-4 spectrophotometer.

REFERENCES

1. M. F. Shostakovskii and A. V. Bogdanova, ZhOKh, 17, 565, 1947.

2. M. F. Shostakovskii, F. P. Sidel'kovskaya, M. G. Zelenskaya, N. N. Shkurina, and T. Ya. Ogibina, Izv. AN SSSR, OKhN, 482, 1961.

3. W. Breitenbach, F. Galinovsky, and H. Neswadba, Mon., 87, 580, 1956.

4. Beilst., 20, 122.

5. K. D. Nenicescu, Organic Chemistry, Vol. 2, [Russian translation], IL, Moscow, 594, 1963.

6. K. W. K. Kohlrausch and R. Seka, Ber., 71, 1563, 1938.

7. R. S. Mulliken, J. Chim. Phys., 61, 20, 1964.

8 August 1966

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