THE FORMATION OF CHARGE-TRANSFER COMPLEXES FROM N-VINYLINDOLE AND CHLORINE, BROMINE, AND IODINE

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The reaction of vinylindole with bromine, chlorine, and iodine in CCl_4 solution in the cold leads to the formation of charge-transfer complexes (CTC). The formation of CTC has been confirmed by a study of the physicochemical properties and the IR and UV spectra of the reaction products.

There is no information at all in the literature relating to the interaction of halogens with compounds in the molecule of which a vinyl group is attached to a nitrogen atom. In the present work we have studied the halogenation of N-vinylindole. If one compares the nitrogen atom in this compound with the oxygen atom in the vinyl ethers, the absence of an unshared pair of nσ-electrons must be noted.

A calculation that we have performed with the aid of a semiempirical variant of the SCF MO LCAO method has shown that the ionization potential of N-vinylindole is lower than the ionization energy of an electron from the top occupied π-electron molecular orbital of an alkyl vinyl ether by approximately 1.2 eV. These results permit the assumption that in the halogenation of N-vinylindole it will be possible to observe some differences from the case of the vinyl ethers, which add chlorine or bromine at the double bond with the formation of α,β-dihaloethyl derivatives [1–3].

We have shown previously that N-vinylindole is readily capable of reacting with chlorine and bromine, forming stable dark red products [4]. In a further, more detailed, physicochemical study of the structure of the halogenation products of N-vinylindole it was found that they are polymeric in nature and that the addition of the halogens to the vinyl group is unlikely. A strong indication of the opening of the double bond of the vinyl group to form a polymethylene chain is the fact that catalytic amounts of halogen (Cl, Br, I) proved to be capable of causing the polymerization of N-vinylindole. Under these conditions, a product was formed which was identical in properties to the polyvinylindole obtained under the influence of free-radical initiators. The IR spectra of the products of the chlorination, bromination, and iodination of N-vinylindole obtained at equimolecular ratios of the reactants, lack bands in the region of the absorption of the double bond of the $—CH=CH_2$ group (~1640 cm^{-1}) and the symmetrical deformation vibrations of the C—H bonds in methyl groups (~1380 cm^{-1}) and retain frequencies which can be connected with the presence of indole rings (~1610, 1560, 1200–1300, 1020, and 740 cm^{-1}) [5]. On the whole, the nature of these spectra resembles the IR spectrum of polyvinylindole (Fig. 1).

The intense coloration of the halogenation products of N-vinylindole, the high molecular weights and variable composition of the compounds formed, and also the results of a calculation indicating a comparatively low potential of the N-vinylindole molecule, have served as a basis for the hypothesis that in this case the formation of charge-transfer complexes (CTC) takes place. To prove this hypothesis, a study of the electronic absorption spectra of the products of the halogenation of N-vinylindole is very important. As can be seen from Fig. 2, they have a series of new bands in the 350–400 and 450–550 nm region as compared with the absorption of N-vinylindole and its polymer. The latter do not absorb light in the region of wavelengths greater than 300 nm and in the visible part of the spectrum. Molecular bromine, studied under analogous conditions (in dioxane solution) has maxima in the 350–400 nm region. It is extremely likely that one of the bands is due to the absorption of molecular bromine present in a complex and the second is due to the CTC as a whole. In the region of wavelengths less than 300 nm, the halogenation products of N-vinylindole have two absorption bands. If it is assumed that the nature of these bands is the same as for the indole molecule, there is a bathochromic shift of 15–25 nm.

Halogenation of N-Vinylindole at –15° C

Halogen	Ratio of N-vinylindole to halogen, molar	Time, min.	Mp, °C	Mol. wt.		Empirical formula	Halogen, %		Yield, %
				found	calculated		found	calculated	
Cl_2	1 : 0.13*	45				—	—	—	—
Cl_2	1 : 1	60	168—178	995	1000	$C_{60}H_{54}Cl_4N_6$	14.17	14.28	32
Cl_2	1 : 1.5	85	420	—	717	$C_{40}H_{36}Cl_4N_4$	19.08	19.70	31
Br_2	1 : 0.15	160	126—139	2180	2200	$C_{120}H_{108}Br_4N_{12}$	15.69	15.71	67
Br_2	1 : 1	150	252—279	1330	1340	$C_{60}H_{54}Br_6N_6$	36.59	35.87	21
Br_2	1 : 2	40	400	740	760	$C_{20}H_{16}Br_6N_2$	62.86	62.82	90
I_2	1 : 0.12	120	234—249	1340	1366	$C_{60}H_{54}I_4N_6$	36.76	37.30	22

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*No precipitate was formed.

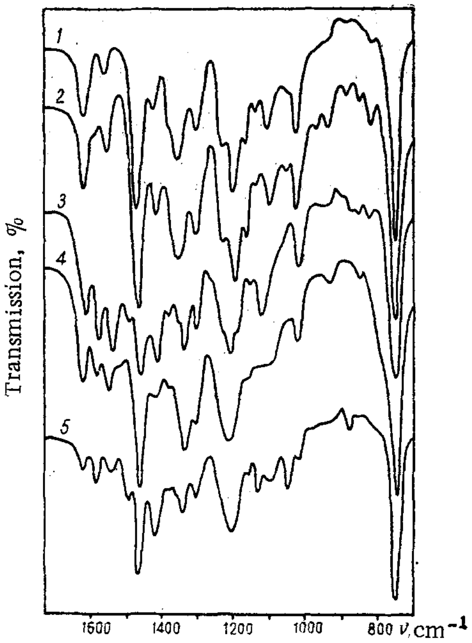


Fig. 1. IR spectra, UR-10 instrument: 1) polyvinylindole obtained with ADIBN catalyst; 2) polyvinylindole obtained in the presence of molecular bromine; 3) product of the reaction of vinylindole with bromine; 4) product of the reaction of vinylindole with chlorine; 5) product of the reaction of vinylindole with iodine.

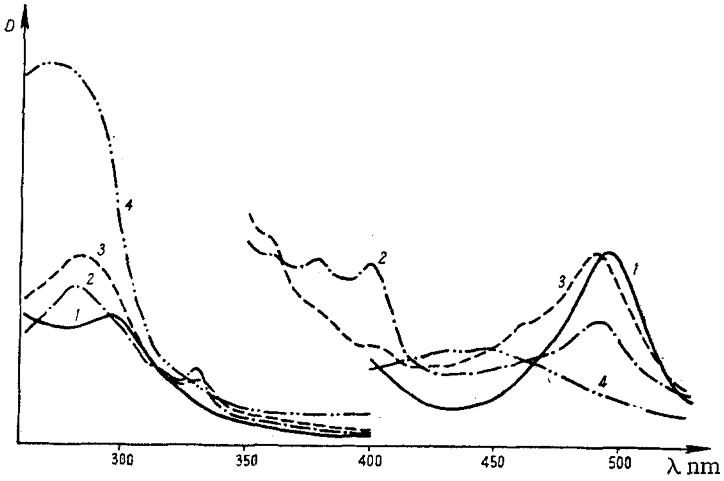
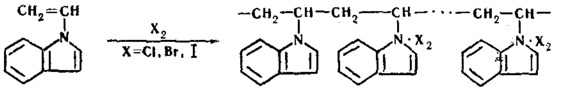


Fig. 2. UV spectra (SF-4 instrument, solvent dioxane): 1) product of the reaction of ethylindole with bromine; 2) product of the reaction of vinylindole with bromine; 3) product of the reaction of vinylindole with chlorine; 4) product of the reaction of vinylindole with iodine.

One of the features of charge-transfer complexes is their capacity for giving an EPR signal [7]. This property is characteristic for all the chlorination, bromination, and iodination products of N-vinylindole that we have studied, while the initial N-vinylindole and its homopolymers do not give an electron paramagnetic resonance signal. Numerous examples are known of the formation of stable complexes with electron-donating compounds as a result of their high polarizability and the presence of vacant orbitals of low energy [6,7]. The capacity of the simplest heterocycles, including pyrrole for giving CTC with halogen-substituted benzenes has recently been reported by M. G. Voronkov et al. [8].

On the basis of a consideration of literature data, and also the experimental investigations that we have carried out, we may consider that the reaction of N-vinylindole with chlorine, bromine, and iodine takes place in accordance with the following scheme:



By making use of the classification developed by Mulliken, the complexes shown in the scheme can be assigned to the nπσ-type, while their structure must be closer to that of the πσ-type than to the nσ-type [9].

The reactions of N-vinylindole with iodine, bromine, and chlorine take place with different intensities. Chlorine is the least active. We have investigated this reaction in carbon tetrachloride solution in the cold. Some of the results obtained are given in the table and in the experimental section of this paper.

As can be seen from the figures in the table, the composition of the products depends on the amount of halogen used in the reaction and on the time of its interaction with the N-vinylindole. At an equimolecular ratio of the reactants or with an excess of halogen, high-melting products containing two atoms of halogen per N-vinylindole link are obtained. A cryoscopic study of their molecular weights in camphor has shown that they are mainly tetra- and hexamers of N-vinylindole, the degree of polymerization of which decreases with an increase in the amount of halogen used in the reaction. The majority of bromine derivatives of polyvinylindole are soluble in acetone and dimethylformamide and, on heating, in butanol, and are hydrolyzed by dilute sulfuric acid. The solubility of the products of the chlorination and iodination of N-vinylindole in many organic solvents and in water is very limited. They are stable to hydrolysis and do not change their properties on being heated from 0 to 100° C in an acid medium in which the concentration of sulfuric acid amounted to 0.5–10% and the time of the reaction varied from half an hour to almost 2 days.

EXPERIMENTAL

Bromination of N-vinylindole. A solution of 2.43 g (~0.015 mole) of bromine in 100 ml of dry carbon tetrachloride was cooled to –15° C and then, with stirring, a solution of 2.17 g (~0.015 mole) of N-vinylindole (bp 71° C (1 mm), n_D^{20} 1.6330) in 50 ml of CCl_4 was added to it over a period of 1 hr and 30 min. The resulting cherry-red precipitate was filtered off, washed repeatedly with carbon tetrachloride, and dried in a vacuum of 2–3 mm to constant weight. This yielded 0.74 g (21%) of a bromination product of N-vinylindole which was soluble in acetone and dioxane and had mp 223–238° C. Found, %: Br 21.79; N 7.88. Calculated for $C_{80}H_{72}Br_4N_8$, %: Br 21.85; N 7.65.

Chlorination of N-vinylindole. A three-necked flask fitted with a mechanical stirrer, reflux condenser, and dropping funnel was charged with a solution of 2.15 g (~0.015 mole) of N-vinylindole in 30 ml of CCl_4, and a current of dry chlorine was passed in at –15° C until absorption ceased. After an hour, the product was treated with CCl_4 and dried. This gave 2.75 g (100% theoretical of a dark red power, mp 142–150° C. Found, %: Cl 17.38. Calculated for $C_{60}H_{54}Cl_5N_6$, %: Cl 17.14.

Reaction of N-vinylindole with iodine. A cooled mixture of 2.01 g (0.014 mole) of N-vinylindole (in 20 ml of CCl_4) and 3.55 g (0.014 mole) of iodine dissolved in 110 ml of CCl_4 formed, in 3 hours, 3.83 g (100% theoretical) of brown crystals with mp 163–166° C. Found, %: C 44.74; H 3.38; I 46.75%. Calculated for $C_{40}H_{36}I_4N_4$, %: C 44.64; H 3.33; I 47.03%.

The products of the halogenation of N-vinylindole, the properties of which are given in the table, were obtained in a similar manner to the experiments described above.

Polymerization of N-vinylindole under the influence of bromine. A tube was charged with 0.73 g (5 mmole) of N-vinylindole, and one drop of bromine was added at 18° C. The temperature rose markedly. After 2 hours, the contents of the tube were dissolved in 9 ml of acetone and reprecipitated with 100 ml of ethanol. This gave 0.36 g (~50%) of a pink powder with mp 192–207° C. Found, %: Br 0.69; N 9.69; mol. wt. 1360. Calculated for $(C_{10}H_9N)_9$, %: N 9.79; mol. wt. 1287.

Polyvinylindole in the form of a light yellow powder with mp 243–260° C was obtained in the usual way with a yield of 54% under the influence of a solution of 0.04 g of iodine in 1 ml of diethyl ether.

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