REACTION OF ALKYL HALIDE SALTS OF NITROGEN-CONTAINING HETEROCYCLES WITH SULFUR DIOXIDE IN AQUEOUS SOLUTIONS

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Complexes of quaternary salts with SO_2 are formed on saturation of aqueous solutions of alkyl halide salts of nitrogen-containing heterocycles with sulfur dioxide. The SO_2 concentration necessary for the precipitation of the complexes increases in the order I < Br < Cl and decreases as the alkyl group attached to the nitrogen becomes larger. The sulfur dioxide in the complexes is bonded through the halide ion by a "charge-transfer" coordinate bond, and their separation into an independent phase is due to a change in the degree of hydration during complexing. Several crystalline adducts are described, and the autooxidation of the SO_2 complex of pyridine methiodide is investigated.

We have recently observed [1] that phase separation involving the formation of a second liquid phase – a heavy, orange liquid with the composition $C_6H_8IN \cdot nSO_2$ $(1 < n < 2)$ – occurs during saturation of aqueous solutions of pyridine methiodide with sulfur dioxide. It seemed of interest to ascertain the nature of the "orange oil" and investigate the reaction of halides of various N-alkylated heterocyclic amines with sulfur dioxide in aqueous solutions.

The experiments demonstrated that the iodides of all of the investigated bases (Table 1) behave similarly. Phase separation is also observed in solutions of bromides and chlorides but only when the cation is sufficiently large and the SO_2 concentration is high. The SO_2 concentration at the start of the separation of a second liquid phase can serve as a criterion for comparison of the tendency of the systems to undergo phase separation.

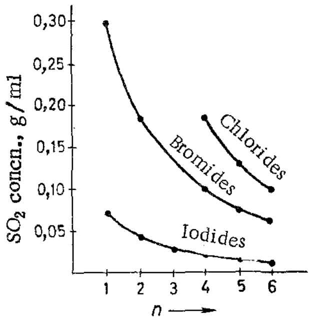

Fig. 1. Dependence of the SO_2 concentration corresponding to the start of precipitation of liquid complexes from 2 M aqueous solutions of N-alkylpyridinium halides on the number of carbon atoms (n) in the alkyl group and on the nature of the halide ion.

The resulting orange (iodides) or light-yellow (bromides and chlorides) liquid products are converted to yellow crystalline substances with an alkyl halide to SO_2 ratio of 1 : 1 when they are cooled in vacuo. In some cases, these crystalline complexes separate immediately upon the action of SO_2 on aqueous solutions of the halide (quinoline and picoline methiodides and quinoline methylbromide).

The absorption spectra of the liquid products are similar to the spectra of known SO_2 complexes of alkali metal iodides [2,3]; they contain a broad band at 250-400 nm, which is characteristic for the coordinate "charge-transfer" bond of halide ions with SO_2 [4].

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TABLE 1. Precipitation of SO_2 Complexes from 2 M Aqueous Solutions of Alkyl Halide Salts of Nitrogen-Containing Heterocycles

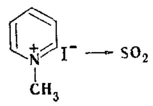
Quaternary salt components		Properties of the precipitated product	SO_2 concn. at start of precip., g/liter
base	alkyl halide		
Pyridine	CH_3I	Orange liquid	69,3
	C_2H_5I	Orange liquid	21,2
	CH_3Br	Yellow liquid	298,0
	C_2H_5Br	Yellow liquid	182,9
	CH_3Cl	No phase separation	—
	C_4H_9Cl	Colorless liquid	180,4
	$(CH_3)_2SO_4$	No phase separation	—
Piperidine	CH_3I	Orange liquid	48,3
	C_4H_9I	Orange liquid	14,1
Nicotinic acid diethylamide	CH_3I	Orange liquid	34,0
	CH_3Br	Yellow liquid	174,2
α-Picoline	CH_3I	Yellow crystals	38,0
	CH_3Br	Yellow liquid	196,3
Quinoline	CH_3I	Yellow crystals	28,0
	CH_3Br	Yellow liquid	144,0
γ,γ'- Dipyridyl	CH_3I	Yellow crystals	44,5
	$C_5H_{11}I$	Orange liquid	31,1
Morpholine	CH_3I	,, ,,	168,0
	C_2H_5I	,, ,,	189,4
	$C_5H_{11}I$	No phase separation	—

TABLE 2. Crystalline SO_2 Complexes of the Alkyl Halide Salts of Some Nitrogen-Containing Heterocycles

Comp.	mp, °C	SO_2 found, %	Empirical formula	SO_2 calc., %
I	68	24,1	$C_7H_{10}BrN \cdot SO_2$	25,4
II	43	20,5	$C_7H_{10}IN \cdot SO_2$	21,4
III	15	21,8	$C_{10}H_{10}BrN \cdot SO_2$	22,2
IV	51	18,9	$C_{10}H_{10}IN \cdot SO_2$	19,1
V	44	21,9	$C_{12}H_{14}I_2N_2 \cdot 2SO_2$	22,5
VI	28	21,2	$C_{14}H_{18}I_2N_2 \cdot 2SO_2$	21,6

The facts enumerated above make it possible to assume that all of these liquids are SO_2 complexes of the alkyl halide salts of the nitrogen bases, solvated with a certain excess amount of SO_2.

The quaternary salt is bonded to the SO_2 molecule through the halide ion:

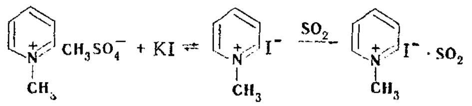


The separation of the SO_2 complexes as an independent liquid phase apparently occurs as a result of a decrease in the hydration of the ion pair during complexing. Of the two centers in it available for solvation by water molecules – the nitrogen atom and the halide ion – the first is shielded by the alkyl group, and the second is shielded by the SO_2 molecule.

An investigation of the reaction of sulfur dioxide with N-alkylpyridinium halides (R from CH_3 to C_6H_{13}), demonstrated that the precipitating concentration of SO_2 increases in the order $I^- < Br^- < Cl^-$ for the same R, while the concentration for a given halide ion decreases as the number of carbon atoms in R increases (Fig. 1). Thus an increase in the hydrophobic properties of the heterocyclic cation and a decrease in the hydration energy in the order $Cl^- > Br^- > I^-$, as well as an increase in the energy of interaction with SO_2 in this sequence, promote the separation of SO_2 complexes.

All of the alkyl halide salts of nitrogen bases, except for morpholine derivatives, are subject to the regularity mentioned above. The separation of SO_2 complexes of N-alkylmorpholinium iodides occurs at higher SO_2 concentrations than in the case of the analogous piperidinium complexes, and the precipitating SO_2 concentration increases as R becomes larger. This anomaly is probably associated with the presence of a second hydration center (the oxygen atom) in the morpholine molecule.

Owing to the great differences in the solubilities of the SO_2 complexes, chlorides, sulfates, and other salts of N-alkyl derivatives of the bases can be converted to the SO_2 complexes of the corresponding iodides. The latter separate out when aqueous solutions of these salts are saturated with sulfur dioxide in the presence of KI:



An interesting peculiarity of the liquid SO_2 complexes of N-alkylpyridinium salts was their tendency to undergo autooxidation in the presence of traces of water. Thus the SO_2 complex of N-methylpiperidinium iodide is converted in a few days to a mixture of oxidation products that does not contain SO_2. The heteroring is not cleaved or oxidized in the process. Only half of the iodide ions are oxidized by SO_2:

$$4C_6H_8IN \cdot SO_2 \xrightarrow{H_2O} (C_6H_8IN)_2 \cdot I_2 + (C_6H_8N)_2SO_4 + S + H_2SO_4$$

The iodine formed is tied up by the remaining half of the pyridine methiodide to give a red, crystalline substance that is resistant to oxidation – N-methylpyridinium polyiodide. The $C_6H_8N^+$ ions that are liberated form the sulfate, and excess SO_2 is oxidized to sulfuric acid. This reaction apparently occurs as a consequence of the specific reaction of the addends in the SO_2 complexes of alkyl halide salts of heterocyclic amines.

EXPERIMENTAL

The alkyl halide salts of heterocyclic amines were prepared by the action of dry alkyl halides on solutions of the bases in benzene or by heating mixtures of the alkyl halides and bases in sealed tubes by the method in [5].

Solutions (2 M) of the alkyl halide salts were saturated with gaseous sulfur dioxide in dropping funnels placed in a thermostat at 20°. This made it possible to remove samples of the solutions and separated oils during the saturation process. The sulfur dioxide content was determined iodometrically, and the halide content was determined from the weight of silver halide precipitated by silver nitrate solution after removal of SO_2 from the weighed sample by refluxing with water.

Reaction of Pyridine Methiodide with SO_2. A stream of SO_2 was bubbled into a solution of 15 g of C_6H_8IN in 20 ml of water. The solution became yellow, and drops of an orange liquid began to separate. The mixture was worked up to give 16.6 g of oil with d_{20} 1.6810. Found: SO_2 28.7%. $C_6H_8IN \cdot SO_2$. Calculated: SO_2 22.5%. The dry residue obtained after decomposition by refluxing with water and vacuum evaporation proved to be pyridine methiodide with mp 115°.

Complex of Pyridine Methiodide with SO_2. When dry SO_2 was passed over thoroughly dried pyridine methiodide, the latter was converted to an orange liquid containing 28% SO_2. The SO_2 content fell to 23% in a cooled (to –10°) desiccator over KOH, but no crystallization was observed. The mass began to crystallize when it was cooled with a dry ice–acetone mixture to –40° to give yellow prismatic crystals with mp 32°. Found: SO_2 22.2%. $C_6H_8IN \cdot SO_2$. Calculated: SO_2 22.5%.

Investigation of the Products of Autooxidation of the SO_2 Complex of Pyridine Methiodide. A 57-g (0.2 mole of $C_6H_8N \cdot SO_2$) sample of the orange oil precipitated by sulfur dioxide from 2 M aqueous pyridine methiodide solution was mixed with 3 g (0.2 mole) of water, and the mixture was stored in a sealed ampule for 1 month at 20°, after which the contents of the ampule were found to be a viscous mixture of yellow and red acicular crystals. The liquid was squeezed out on a glass filter, and the crystals were washed with small portions of water. Sulfuric acid (0.05 mole), 0.05 g-ion of SO_4^{2-}, and 0.1 g-ion of N-methylpyridinium salt were detected in the liquid and wash waters; I^- ions were absent. The N-methylpyridinium cation was precipitated as the SO_2 complex of its iodide by saturation of the solution with sulfur dioxide in the presence of KI. The complex was decomposed, and the methiodide was isolated. The solid material was extracted with hot ethanol, and the yellow ethanol-insoluble residue proved to be elementary sulfur (0.04 g-atom).

Cooling of the ethanol solution gave 30 g of red prismatic crystals with mp 80°. Heating of the crystals with water resulted in the splitting out of iodine, which can be titrated with thiosulfate. After removal of the "cleavable" iodine by steam distillation, an equal quantity of iodide ion was detected in the residue. Evaporation gave N-methylpyridinium iodide. Found: C_6H_8IN 63.4; I_2 36.5%. $(C_6H_8IN)_2 \cdot I_2$. Calculated: C_6H_8IN 63.6; I_2 36.4%.

The crystalline SO_2 complexes (Table 2) of 2-picoline methylbromide (I), 2-picoline methiodide (II), quinoline methylbromide (III), quinoline methiodide (IV), and γ,γ'-dipyridyl methiodide and ethiodide (V,VI) were obtained by saturation of solutions of the appropriate salts at 20° with sulfur dioxide. In the case of I, III, and VI, a liquid initially separated from the solutions and in time began to crystallize. The remaining adducts crystallized immediately from solution. The melting points were determined in sealed capillaries.

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