

AgHal Crystals Growth Modification and Stabilization by the Amides of Phosphoric Acid

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Summary

Synthetic approach to the titled compounds is based upon the reactions of nitrogen containing heterocyclic compounds with phosphoric anhydride. The amides of phosphoric and pyrophosphoric acids showed to be powerful silver bromide and mixed silver halides crystals growth modifiers in the model and industrial photographic emulsions. The correlation analysis molecular structure - modifying activity made it possible to work out the principles of target orientated synthesis of efficient AgHal crystals growth modifiers. The specific features of the modifiers adsorption on the microcrystals surface are discussed.

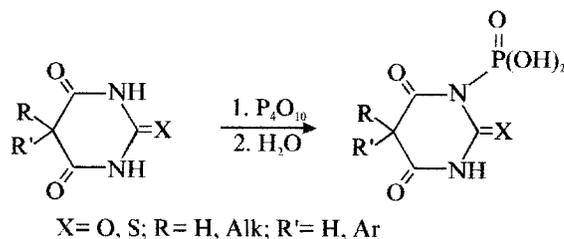
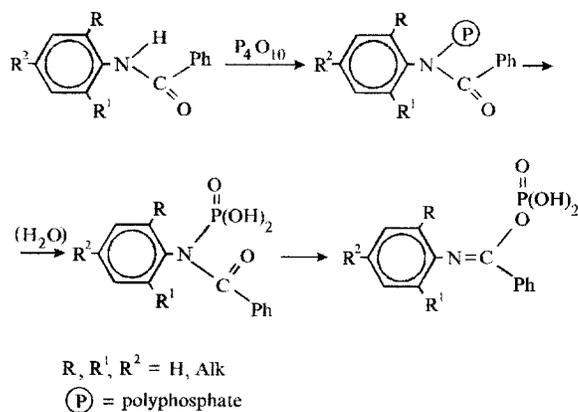
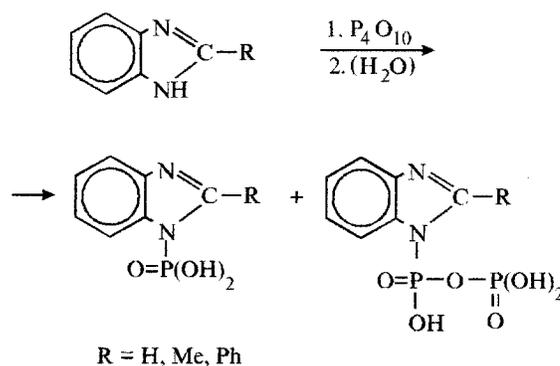
Results and Discussions

Modification of silver halides photographic emulsions^{1,2} is a widely used technological approach to highly sensitive films and papers. A good number of recent decade studies presented mostly in patents were devoted to various types of compounds with AgHal microcrystals modifying activity. Predominantly these compounds are heterocyclic preferably nitrogen containing aromatic systems. Nevertheless up to now it is impossible to work out a reliable correlation between the molecular structure of modifiers and their modifying activity.

The main target of our research was to synthesize series of potential AgHal crystals growth modifiers with some similar structural features for revealing a correlation molecular structure-modifying activity. The compounds under study were azoles, acyclic and cyclic amides that contained the N-P(O)(OH)₂ or N-P(O)(OH)-O-P(O)(OH)₂ fragments. The modifying activity of such compounds was compared with that of nonphosphorylated precursors.

Azoles acyclic and cyclic amides were phosphorylated by phosphoric anhydride in chloroform.^{2,4} In all cases the primary attack by P₄O₁₀ was directed towards the most nucleophilic nitrogen atom. The following mild treatment with water split up the residual polyphosphoric fragments and gave corresponding amides of phosphoric or pyrophosphoric acids. For azoles, acyclic amides and thiobarbituric acid there was determined either reversible or irreversible N

→ O (S) migration of the phosphoryl group (phosphotropy).



The modifying activity of the synthesized compounds and their nonphosphorylated analogues was studied in the model and industrial black-and-white and colour AgBr AgCl,

AgClBr and AgBrI emulsions. The emulsions were prepared by two-jet technology with the control of all main conditions. The modifiers were introduced in two steps, the first portion (0.25) was added to the initial cubic emulsion in one go and the rest of modifier was added with potassium halide during the second step of emulsification. Efficient modification of emulsions did not need specific conditions, everything had been done according to the existing technological processes except somewhat prolongation of the procedure.

The majority of the compounds exhibited modifying activity towards model silver bromide emulsions. According to electronic microscopy the resulting emulsions contained various for different modifiers rhombododecahedral and/or round shaped microcrystals. The shape of microcrystals depended not only upon the nature of modifiers but their concentration as well. The most active modifiers were azoles and among those phosphorylated benzotriazole exhibited the most advanced properties. The concentration of benzotriazolyl phosphoric acid was varied between 100 and 400 mg/Ag g-atom. The maximum population of rhombododecahedral micro-crystals (above 90%) was achieved with the modifier concentration above 200 mg/Ag g-atom. The concentration of benzotriazolyl phosphoric acid higher than 300 mg/Ag g-atom did not induce any further modification of AgBr microcrystals. The concentration 200 mg/Ag g-atom was determined to be the optimum for the highest sensitivity data of the modified emulsion.

Modification of industrial emulsions by benzotriazolyl phosphoric acid exhibited similar features, i.e. efficient formation of rhombododecahedral microcrystals with the optimum concentration 200 mg/Ag g-atom. The higher concentration depressed emulsions sensitivity probably due to the shielding effect of molecules of modifiers absorbed on the microcrystals surface.

Table 1. Photographic data of the control and modified Ag Br model emulsions

\tilde{N} , mg modifier/Ag g-atom	S	γ	D_0
0	12.0	4.5	0.12
100	25.0	5.0	0.03
200	37.0	4.0	0.02
300	29.0	4.7	0.05

The other parameters for the process of modification including temperature, pAg, pHal, etc were studied as well. The specific features of modified by the phosphorylated azoles emulsions were not only significantly higher than the control sensitivity but antifog and pronounced stabilizing effects as well (Table 1)⁶. There were studied various kinds of modified emulsions sensitization. Sulfur-gold sensitization gave the best results (Tables 2, 3).

Phosphorylated pyrimidinetriones exhibited a distinctive modifying activity in photographic emulsions with tabular microcrystals.

Table 2. Time-dependant lipening of the control AgBrCl emulsion under sulfur-gold sensitization

Photo-graphic data	Time, min				
	30	60	90	120	150
$S_{0.85}$	10.0	22.0	35.0	42.0	38.0
γ	4.4	4.4	4.4	4.6	4.6
D_0	0.05	0.22	0.25	0.43	0.55

Table 3. Time-dependant ripening of the modified AgBr(I) emulsion under sulfur-gold sensitization

Photo-graphic data	Time, min				
	30	60	90	120	150
$S_{0.85}$	65.0	82.0	105.0	120.0	111.0
γ	4.2	4.8	5.2	5.5	5.2
D_0	0.08	0.11	0.14	0.18	0.20

It was determined by means of solid state ¹³C NMR spectrometry that the aromatic rings are of insignificant influence upon adsorption of organic compounds on the surface of AgHal microcrystals whereas the ³¹P NMR spectra of the adsorbed and nonadsorbed species varied vividly. Hence the phosphorus containing fragments were the most forcible part of the modifiers molecules in the process of adsorption. This effect explains well the lower modifying activity of nonphosphorylated compounds than their phosphorylated derivatives. In the range of concentrations used the modifiers adsorbed on silver halides microcrystals reversibly.

The most active phosphorylated crystals growth modifiers acted as efficient stabilizers. The stabilizing effect of benzotriazolyl phosphoric acid was much higher than that of benzotriazole.

On the basis of the experimental data we have worked out the main principles for target orientated synthesis of active crystal growth modifiers. These are:

1. AgHal crystal growth modifiers need to be cyclic or compact acyclic compounds containing three or more n-electrons centres for an efficient interaction with the subsurface silver cations.
2. The crystals growth modifiers are not necessarily the aromatic compounds. The best adsorbates towards AgHal microcrystals are those with distinctive steric lability, in other words the compounds that can easily adopt on the crystals surface.
3. Tautomeric (prototropic, phosphorotropic) equilibria in the adsorbates molecules can promote the modifying activity of organic compounds.
4. Introduction of the dihydroxyphosphoryl or trihydroxyphosphoric groups in the modifiers molecules should enrich the possibility of their interaction with the subsurface silver cations on one

hand and electrophilic phosphorus atoms with halogens anions on the other hand.

References

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