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PREPARATION OF CRYSTALLINE SALTS OF METHYLPHENAZINIUM RADICAL CATION

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A stable crystalline salt (e.g. perchlorate) of the methylphenazinium radical cation was prepared. The method is based on the photoreduction of phenazine methosulfate in acid solution containing oxalate or tartrate.

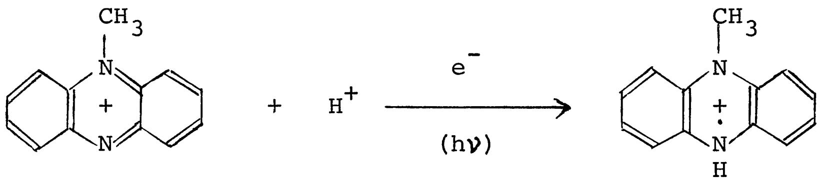
Although a number of works[1-3] have been carried out on the chemical or the biochemical production of the methylphenazinium radical cation ($MPH^{\dot{+}}$) from methylphenazinium (MP^+) methosulfate[4] in solution, there seems to be no published work on the preparation of a stable radical salt of $MPH^{\dot{+}}$ in its crystalline form. We have found a simple method for the preparation of crystalline radical salts, which is based on the photoreduction of MP^+ in the presence of a certain anion such as oxalate or tartrate. Pure crystalline perchlorate of the radical cation can be prepared by replacing the counter anion of the so obtained radical salts. A typical procedure for the oxalate and the perchlorate preparation is as follows.

PMS (100 mg), obtained from Sigma Chemical Co., was dissolved[5] in 8 ml of 1/2 M oxalic acid, to which 2 ml of freshly prepared 1/12 M ascorbic acid solution was added. After being exposed to visible light[6] at room temperature, the green colored reaction mixture was kept in a refrigerator overnight. The dark green product was washed with cold water and dried. The needle-shaped oxalate crystals thus obtained were redissolved in a minimum volume of 1/20 M oxalic acid at 50°C, to which an excess of sodium perchlorate solution (50mg/ml) was added untill no more precipitates were produced. The precipitates were gathered and washed with ether containing 10 % of acetone. When necessary, recrystallization was followed.

The result of elemental analysis for the perchlorate preparation shows a fair agreement with that expected for $MPH^{\dot{+}}$ perchlorate$^-$ ($C_{13}H_{12}N_2ClO_4$). Found: C 52.99%; H 3.94%; N 9.70%; Cl 11.77%. Calculated for $C_{13}H_{12}N_2ClO_4$: C 52.80%; H 4.09%; N 9.47%; Cl 11.99%. The presence of the ring NH in the perchlorate salt was verified by an absorption at ~2600 cm^{-1} in the IR spectrum, which had been absent in the starting $MP^+CH_3SO_4^-$. A further evidence for the production of the $MPH^{\dot{+}}$ radical salt was given from the ESR spectrum of the perchlorate crystals which show in absolute alcohol a composite hyperfine structure identical with that of $MPH^{\dot{+}}$ produced by the chemical reduction of MP^+.[3] From the characteristic optical absorption of $MPH^{\dot{+}}$ at

450 nm ($\varepsilon = 2.63\text{x}10^4$),1) the purity of perchlorate was estimated to be larger than 95 %. The radical salts are stable for several months, even if kept in air at room temperature.

All the foregoing results indicate that the photoreduction of MP^+ takes place according to the following scheme:



Methylphenazinium ion (MP^+)

Methylphenazinium radical ion ($MPH^{+\cdot}$)

The above reaction was found to take place in an acid solution (pH = 1-6), even with acetate or chloride as counter anion as well as with tartrate, oxalate, or perchlorate. However, the preparation of radical crystals is limited to certain anions, such as oxalate and tartrate. Presumably the small solubility product of $MPH^{+\cdot}$ with these anions favors immediate precipitation as crystals. At a relatively high pH (pH = 4-6), the radical crystals are produced in the absence of ascorbic acid. At a lower pH (pH $<$ 3), however, the presence of ascorbic acid is effective in obtaining a good yield of the crystals. Detailed mechanism of the reaction including the identity of the electron donor to MP^+ is still obscure at present.

ESR spectra of these radical salts in the crystalline state show strongly narrowed singlets ($\Delta H_{msl} < 1$ G), indicating an extensive exchange interaction between the radical ions. The magnetic susceptibility of the perchlorate crystals was found to show a complicated temperature dependence, with an extremely low paramagnetic contribution for all the temperature range between 4.2 and 300°K. Detailed magnetic properties of these radical crystals as well as the mechanism of the photoreduction of MP^+ will be subjects of future publication.

References

1) W. S. Zaugg, J. Biol. Chem., 239, 3964 (1964).

2) J. R. White and H. H. Dearman, Proc. Nat. Acad. Sci. U.S., 54, 887 (1965).

3) K. Ishizu, H. H. Dearman, M. T. Huang, and J. R. White, Biochemistry, 8, 1238 (1969).

4) Commonly called phenazine methosulfate (PMS).

5) All the solutions were bubbled with nitrogen gas prior to use and after each mixing.

6) Usually with a 15 Watt fluorescent lamp at a distance of 10 cm for 40-60 min.

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