Table II. Interrupted Reactions of 3-Chloropyridine-*d* with $NaNH_2$ in Ammonia[a]

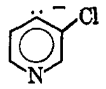
Position of D	Atom % D[b] Initial	Atom % D[b] Final	% Cl^- Formed
2	61	61	30
4	75	20	46

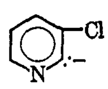
[a] A molar excess of $NaNH_2$ was employed and the reaction was quenched after about 15 min by the addition of solid NH_4NO_3 to a solution at reflux. [b] Reproducibility of the nmr analyses is ±5%.

in the quantity of D-4 under conditions leading to extensive chloride ion formation.[13] In marked contrast there is no detectable change in the amount of D-2 label even after 30% chloride ion is liberated.

Our observations may be rationalized in terms of a 3-chloro-4-pyridyl anion intermediate (VIII) which reacts by two competing processes. Formation of this anion may occur by base-catalyzed proton abstraction from the 4 position of I. The anion may react by chloride ion loss to give pyridyne III or by proton capture from solvent to regenerate substrate I and base. When hydrogen isotopes are employed, the exchange process becomes observable. In methanol, proton exchange is overwhelmingly favored over chloride ion loss, but in the less acidic ammonia both reactions are observed. The extent of 3,4-pyridyne formation relative to hydrogen exchange is largely determined by solvent acidity; the latter reaction becomes increasingly important as the protonating ability of the solvent increases.

This mechanism ought to apply to the formation of II from I by a 3-chloro-2-pyridyl anion (IX). However, no evidence exists for the formation in detectable quantity of IX or even for the conversion of I to II. If II were to be formed from IX, it then is understandable why there is no evidence for this pyridyne. The shortcoming of our interpretation is that it does not account for the preferred position of exchange in I.


VIII


IX

More needs to be known about H–D exchange in pyridines. This area of investigation presently is characterized by a paucity of data and seemingly divergent observations. An excellent illustration of the latter is H–D exchange in pyridine itself.[10a,14] We shall shortly report kinetic data on D–H exchange for some halopyridines and their N-oxides.

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(13) The extent of D–H exchange and chloride ion loss is not unlike that for chlorobenzene under similar conditions. See ref 12 and references cited therein.

(14) I. F. Tupitsyn and N. K. Semenova, *Tr. Gos. Inst. Prikl. Khim.*, **49**, 120 (1962); *Chem. Abstr.*, **60**, 6721c (1964).

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Received August 8, 1966

Book Reviews

Methods of Quantum Chemistry. By M. G. Veselov, Leningrad State University, Leningrad, U.S.S.R. Academic Press Inc., 111 Fifth Ave., New York, N. Y. 1965. xi + 181 pp. 15.5 × 23.5 cm. $7.50.

The book contains five review articles by Russian authors on the determination of molecular wave functions. Two of the articles are based on papers presented at the first Soviet Conference on Quantum Chemistry in 1961 and the other three were apparently written in 1962.

In the first chapter Rebane gives a brief review of the "Atoms in Molecules" and the "United Atoms" methods for diatomic molecules and a comparison of the relative merits of the two approaches.

The second chapter is a discussion by Mestechkin of the Hartree–Fock method, the Roothaan SCF–LCAO theory, and the Hückel method. This chapter contains very little material that cannot be found elsewhere, but its merit is that these various methods are combined in a logical way. In a few places the author expresses his personal opinion; of particular interest is the remark on page 65 that the LCAO method is better justified for the σ bonds than for the π electrons. It should be realized that Mestechkin wrote this in 1962 and that he predicted many recent developments in the extended Hückel LCAO theory.

The third chapter contains a study of the chemical properties of conjugated and aromatic molecules based on the Hückel LCAO method by Tupitsyn and Adamov. We found nothing in this chapter that has not already been presented in one of the many books on MO theory for organic chemists. For example, in Streitwieser's book this topic was discussed much more extensively.

In the fourth chapter Nikitin attempts to apply some of the theories for many-electron systems that were developed in solid-state physics to long conjugated molecules. The conclusions are of a very general nature and they do not indicate that these physical methods will solve many chemical problems in detail.

The last chapter, by Rebane, is entitled "Application of the Method of Finite Differences to Problems in Molecular Orbital Theory." This is a method for solving secular equations by first combining the atomic orbitals to Bloch functions or similar functions. We agree with the author that this method is but little known among quantum chemists and that it is hard to find it in the literature.

The most interesting aspect of the book is that it shows us how some Russian scientists judge the existing theories on molecular wave function determination. All five articles are well written and in many places they give us a fresh outlook on quantum chemical methods. However, the bulk of the material is not new and is beginning to be outdated. We feel that the publication of five-year old review articles is of little use to the scientific community if a large number of up-to-date reviews in the field are already available. Needless to say that the responsibility for this lies with the publisher and not with the authors.

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