

THE REACTIVITY AND STRUCTURE OF NITROGEN DIOXIDE

PETER GRAY

University Department of Chemical Engineering, Cambridge, England

AND

A. D. YOFFE¹

Weizmann Institute of Science, Rehovoth, Israel

Received May 27, 1955

CONTENTS

I. Introduction.....	1070
II. Preparation of nitrogen dioxide.....	1072
A. From concentrated nitric acid and copper.....	1072
B. From lead nitrate.....	1072
C. From nitrous and nitric anhydrides.....	1072
D. From the nitrosyl ion and the nitrate ion.....	1072
E. From nitric oxide and oxygen.....	1073
III. The equilibrium $N_2O_4 \rightleftharpoons 2NO_2$	1075
A. Equilibrium in the gas phase.....	1075
B. Equilibrium in the liquid and solid phases.....	1077
C. The rate of attainment of the equilibrium $N_2O_4 \rightleftharpoons 2NO_2$ in the gas phase..	1078
IV. Physical properties of the equilibrium mixture.....	1079
A. Solid nitrogen dioxide.....	1079
B. Liquid nitrogen dioxide.....	1080
C. Gaseous nitrogen dioxide.....	1083
V. Physical properties of the individual species (NO_2 , N_2O_4).....	1085
A. Nitrogen dioxide monomer.....	1085
B. Dinitrogen tetroxide.....	1087
VI. Structural relations between nitrogen dioxide and its derivatives and the structure of dinitrogen tetroxide.....	1088
A. The series NO_2^+ , NO_2 , NO_2^- , and NO_2^{2-}	1088
B. The series XNO_2 and $YONO$	1090
C. The structure of dinitrogen tetroxide.....	1090
VII. The reactions of nitrogen dioxide.....	1093
A. General considerations.....	1093
B. The association of nitrogen dioxide with other radicals.....	1094
C. Addition of nitrogen dioxide to unsaturated compounds.....	1097
D. Hydrogen-abstraction reactions.....	1102
E. Metathetical reactions.....	1107
1. Oxidation by nitrogen dioxide.....	1107
2. Reduction by nitrogen dioxide.....	1110
3. The decomposition of nitrogen dioxide.....	1111
F. Flames supported by nitrogen dioxide.....	1113
G. Nitrogen dioxide as a catalyst: sensitization of chemical reactions and explosive ignition.....	1115
H. Photochemistry of nitrogen dioxide.....	1116

¹ Present address: Department of Physical Chemistry, University of Cambridge, Cambridge, England.