Table 1. Kinetics of ester-interchange between methyl acetate and ethanol. Vairation of specific reaction rate (k) with temperature.

Temperature (°C)	80	85	90	95	100	105
Specific reaction rate k (10^{-8} l/mole-sec)	5.91	8.62	12.3	15.0	21.1	29.6

The experiment was repeated at several temperatures in the range 80 – 105° (Ref. Table 1).

From the results the energy of activation was evaluated to be 16.7 kcal/mole and the entropy of activation to be – 44.3 cal/deg. mole.

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[1] J. D. ROBERTS and M. C. CASERIO, Basic Principles of Organic Chemistry, W. A. Benjamin, Inc., New York 1965, p. 532.

[2] A. N. PUDOVIK, R. A. CHERKASOV, and R. M. KONDRATEVA, Vysokomol. Soedin, Ser. A **9** (5), 1118 [1967].

[3] J. HRIVNAK, Z. VESELA, E. SOHLER, and J. DRUBEK, Chem. Prumysl. **15** (1), 7 [1965].

[4] H. J. ARNIKAR, T. S. RAO, and A. A. BODHE, J. Chromatog. **47**, 265 [1970].

[5] P. LORRAINE, P. ROWLAND, MACK, H. CHARLES, COLL, and E. EMERY, J. Gas Chromatog. **6** (3), 173 [1968].

[6] V. PETERKA, ZBIROVSKY, and MIROSLAV, Collect. Czech. Chem. Commun. **35** (3), 1010 [1970].

Excitation of N_2^+ by Vibrating Nitrogen Molecules

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Flowing nitrogen gas, bombarded by 50 keV electrons, emits the first negative and second positive bands. Operation of a microwave discharge upstream enhances the former, but not the latter: this is shown to be due to conversion of vibrational excitation in N_2 into electronic excitation in N_2^+.

OLDENBERG[1] has reviewed excitation processes in nitrogen discharges and afterglows. The B → X, first negative bands of N_2^+ are directly excited from N_2 in the negative glow of a d.c. discharge (or when nitrogen is bombarded by past particles). In low frequency[2] and microwave discharges[3] there is evidence of indirect excitation; the best evidence of such processes comes from a study of the pink afterglow (P.A.) by BRÖMER and DÖBLER[4], who showed that the population rate of $N_2^+(B)$ is greater than the ionisation rate. Some plausible processes are:

$$N_2^+(X) + N_2^\dagger \rightarrow N_2^+(B) + N_2\,, \tag{1}$$

$$N_2^+(X) + e \rightarrow N_2^+(B) + e\,, \tag{2}$$

$$N_2^+(X) + N_2^m \rightarrow N_2^+(B) + N_2\,, \tag{3}$$

$$N + N_3^+ \rightarrow N_2^+(B) + N_2\,. \tag{4}$$

N_2^m, $N_2^\dagger$ represent metastable, electronically-excited and ground state, vibrationally excited N_2, respectively. The processes may well be complex; e. g. (1) may involve step-wise vibrational excitation of N_2^+ followed by collisional conversion between the X, A and B states.

Interconversion of nitrogen ions (N^+, N_2^+, N_3^+, N_4^+) does occur in nitrogen afterglows[5, 6] but there is no evidence that (4) leads to excitation of N_2^+; it appears to be ruled out by the absence of N_2^+ emission from an auxiliary discharge in the Lewis-Rayleigh afterglow[3]. The other three processes are less easily distinguished because of the case of exchange of energy between these species. For example, in afterglows, process (5)[7] leads to rapid equilibration between the energy distributions of $N_2^\dagger$ and electrons:

$$N_2^\dagger + e \rightleftharpoons N_2 + e\,, \tag{5}$$

i. e. (1) is not easily distinguished from (5) followed by (2).

The study[8] of electron beam excitation of nitrogen has therefore been extended to gas flowing from a microwave discharge: this is known to contain high concentrations of $N_2^\dagger$[9]. Though still complicated, the excitation processes are likely to be simpler than in the discharge or the P.A.

“Oxygen-free” nitrgen (British Oxygen Gases) was used: ready production of the P.A. indicated adequate purity. Before reaching the electron-beam cell, the gas flowed through a straight silica tube, 10 mm i. d.; the position of the microwave cavity could be adjusted along this tube to give distances of 15 – 120 cm between it and the cell. Electrons accelerated to 50 keV *in vacuo* passed through a thin aluminum foil[8] into the nitrogen stream at right angles to the flow. Successful preliminary experiments were carried out in a pyrex cell similar to that used before[8]: it was a cylinder, 3 cm in diameter, the flowing gas entering and leaving through 1 cm diameter side tubes; however, the flow pattern in the cell was uncertain and the P.A. often appeared in the cell. Better results were obtained with a continuous flow tube with 1 cm diameter side arms carrying the electron beam: this reduced the beam current (maximum reached was 1.6 μA) and the luminescence was weak. Light emitted at right angles to both flow and beam was analysed with a Bausch and Lomb $f/4$ grating monochromator (33-86-02)

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and an E.M.I. 9558Q photomultiplier. Corrections were made for scattered light from the discharge.

The microwave discharge produced the yellow Lewis-Rayleigh discharge downstream, but it did not interfere with measurements in the ultra-violet. The P.A. appeared over a distance of several cm, separated from the discharge by a dark space; the P.A. was much brighter than the beam luminescence. At the low pressures used, both first negative and second positive band systems were relatively strong in the electron beam; first positive was very weak [8]. Because of the low intensity, measurements were concentrated on the first negative $(0-0)$ band at 3914 Å and the neighbouring second positive bands. When the discharge was switched on, the latter were hardly affected, but the intensity of first negative increased: the enhancement is expressed as the ratio of intensities with and without the discharge. In a typical experiment, a pressure of 7 Torr and a measured linear flow-rate of 4.2 m s^{-1} were used (the actual flow rate must be greater when the discharge is on because of heating of the gas). The enhancement factor was 6 at 30 cm from the discharge (just downstream of the P.A.) and it fell steadily to 1.4 at 120 cm. The enhancement was greater at higher flow rates and with increasing pressure it increased to a maximum at 7 Torr and then decreased slowly. For example, at 25 Torr (no P.A. visible) enhancements of 4 and 2 occurred at 20 and 40 cm below the discharge respectively. The first negative intensity was proportional to the electron beam current between 0.2 and 1.6 μA.

In nitrogen at 7 Torr and 300 K, a 1 μA electron beam alone will produce ions at $\sim 2 \cdot 10^{13}$ cm^{-3} s^{-1}: 10% will be excited in the B state and only 15% of these will emit because of collisional deactivation [8]. An enhancement factor of 6 corresponds to a photon emission rate from the B state of $\sim 2 \cdot 10^{12}$ cm^{-3} s^{-1}; i. e. the intensity with the beam alone can be used to calculate the absolute yield. (Uncertainties due to the cell geometry are considerable but cancel when the luminescence rate is compared with the ionization rate.) To estimate the ion concentration, the rate of loss is needed: estimates for various processes (downstream flow, recombination etc.) suggest that the dominant loss process is ambipolar diffusion to the walls, especially when the discharge is on because of electron heating by (5). An estimate of ion and electron concentrations of $1-5 \times 10^8$ cm^{-3} appears reasonable (cf. 5×10^9 in the P.A. [10]). In addition to N_2^+, the discharge introduces nitrogen atoms and metastables: the density of the $N_2(A)$ state is $\sim 2-4 \times 10^9$ cm^{-3} [11]. A similar value for the a′ state can be calculated from its deactivation rate [6] if it is produced efficiently from N atom recombination: concentrations of other states should be smaller. The discharge will also raise the kinetic temperature, but this alone would cause a small reduction in the first negative intensity: at constant pressure, the density will decrease, and the excitation rate and collision rate will both fall, depending on T^{-1} and $T^{-\frac{1}{2}}$ respectively.

From the values above, process (3) would require a cross-section of $\sim 10^{-11}$ cm^2. The cross-section of (2) is known [12]: it would account for only 1% of the observed intensity even if all the electrons had sufficient energy: also the intensity would depend on the square of the beam current, contrary to observation. So (2) and (3) can be ruled out: they are probably not important in the P.A. either, but (2) will become significant at higher ion densities e. g. in some discharges. The plausibility of (1) has been discussed previously [3]. It accounts for the present observations: the effect of flow-rate and the initial increase with pressure are due to the loss of vibrating molecules to the tube walls. At higher pressures, production of vibrating molecules in the dicharge must become less efficient because of the higher mass flow-rate: the P.A. also appears, then disappears with increasing pressure.

In addition to demonstrating the occurrence of (1), the original aim of this work was to measure the rate constant of the process.

An order of magnitude estimate of 2×10^{-15} cm^{-3} s^{-1} can be made for the region just below the P.A.; this is reasonable if the vibrational temperature is $\geqq 3000$ K. In an attempt at measuring this temperature, a study of the heat content of the flowing gas was made, but no consistent interpretation was possible. This is probably due to the failure of the vibrational energy to follow a Boltzmann distribution under these conditions [13]: when the kinetic temperature falls well below the "vibrational temperature", an anharmonic oscillator will take up a distribution in which the population of higher levels will greatly exceed that expected by a logarithmic extrapolation from lower levels. Evidence for this redistribution as the gas cools between discharge and P.A. was found in these experiments: the "dark space" could be extended by working at high flow-rates: at 7 Torr and 15 m s^{-1}, an enhancement of 7 was observed 10 cm above the P.A. (15 cm below the discharge) and this *increased* to 15 at 2 cm above the P.A. In the "dark space", the Lewis-Rayleigh afterglow is weak, and it was possible to study the first positive bands: enhancement by the discharge was again observed and it increased as the P.A. was approached: this can also be ascribed to the redistribution, since the Franck-Condon factors for the transition, $B \leftarrow X$, favour excitation of the first positive bands in the visible from high vibrational levels. The electron beam excitation is not strong enough for detailed spectroscopic studies and the increasing enhancement of the first negatve bands in the dark space could be due to a decrease in the ion loss rate with increasing density. However, spectroscopic studies [14] with an auxiliary, radio-frequency discharge have demonstrated that the redistribution does occur in this region.

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[1] O. OLDENBERG, J. Opt. Soc. Amer. **61**, 1092, 1098 [1971].
[2] H. H. BRÖMER and F. SPIEWECK, Z. Phys. **184**, 481 [1965].
[3] B. BROCKLEHURST and R. M. DUCKWORTH, J. Phys. B **1**, 990 [1968].
[4] H. H. BRÖMER and F. DÖBLER, Z. Phys. **185**, 278 [1965].
[5] H. H. BRÖMER and J. HESSE, Z. Phys. **219**, 269 [1969].
[6] A. R. DEMONCHY, Thesis, University of Amsterdam 1970.
[7] I. R. HURLE, J. Chem. Phys. **41**, 3592 [1964].
[8] B. BROCKLEHURST and F. A. DOWNING, J. Chem. Phys. **46**, 2976 [1967].
[9] A. M. BASS, J. Chem. Phys. **40**, 695 [1964]. — Y. TANAKA, F. R. INNES, A. S. JURSA, and M. NAKAMURA, J. Chem. Phys. **42**, 1183 [1965].
[10] S.-L. CHEN and J. M. GOODINGS, J. Chem. Phys. **50**, 4335 [1969].
[11] J. A. MEYER, D. W. SETSER, and W. G. CLARK, J. Phys. Chem. **76**, 1 [1972].
[12] A. R. LEE and N. P. CARLETON, Phys. Lett. **27 A**, 195 [1968].
[13] B. BROCKLEHURST, Nature Phys. Sci. **236**, 12 [1972] and references therein.
[14] J. ANKETELL and B. BROCKLEHURST, unpublished work.

Low-temperature Heat Capacity and Paramagnetic Susceptibility Measurements on some Tetragonal Nickel(II) Compounds

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Zero-field splittings have been determined for the spin triplet ground state of Ni(II) in Ni(pyrazole)$_4$Cl$_2$ and Ni(pyrazole)$_4$Br$_2$, by means of heat capacity measurements in the 1—80 K region and by paramagnetic susceptibility measurements in the 2—80 K region.

The results of both measurements can be fitted with theory using the spin Hamiltonian

$$H = g\,\beta\,H\,S + D[S_z^2 - S(S+1)/3] + E(S_x^2 - S_y^2)$$

with the parameter D equal to 7.2 cm^{-1} for the chloride and 5.4 cm^{-1} for the bromide. The value of E appeared to be close to zero for both compounds, indicating nearly axial symmetry.

The anisotropic g-values (calculated from the susceptibility) are $g_\perp = 2.21 \pm 0.03$ and $g_{||} = 2.14$ for the chloride and $g_\perp = 2.20$, $g_{||} = 2.12$ for the bromide.

Introduction

Nickel(II) ions (3d^8) with axially distorted octahedral coordination are known to yield a spin splitting of the ground state (^{3}A$_{2g}$), even in the absence of a magnetic field [1]. Usually these splittings are of the order of 0.1—1.0 cm^{-1} and are caused by second-order pin-orbit coupling. The magnitude of this splitting, D, deends upon the orbital splittings in the excited states (l. c. [1, 2]).

LIEHR and BALLHAUSEN [3] derived D from the orbital splittings by means of the relation $D = -9\,k\,\lambda^2/\Delta^2$, with k = the magnitude of the trigonal ^{3}T$_{2g}$ splitting, λ = spin-orbit coupling constant and Δ = distance between the ^{3}A$_{2g}$ and ^{3}T$_{2g}$ term. In a previous study [4–6] on the spectra, structure and bonding of tetragonal pyrazole compounds, we found unusually large orbital splittings for a number of compounds Ni(ligand)$_4$(anion)$_2$. This would yield zero-field splitting much larger than 1 cm^{-1}, using the relation of LIEHR and BALLHAUSEN [3].

In order to examine if a relation exists between D, the orbital splitting and the nature of the ligand and the anion, we determined D-values for a number of compounds of formula NiL$_4$X$_2$, in which L is a pyrazole or imidazole ligand, and X is a halide or nitrate anion. The D-values were determined with the aid of specific heat and paramagnetic susceptibility measurements. The results for two typical examples are discussed in the present paper.

Experimental

Ni(pyrazole)$_4$Cl$_2$ and Ni(pyrazole)$_4$Br$_2$ were prepared from the metal salt hydrates by adding the ligand in the ratio 1 : 4 in ethanol as a solvent. The compounds were checked for purity by chemical analysis. The crystal structures of both compounds have been published [7, 8].

The heat capacity measurements were performed with the usual heat pulse method. To cool the sample to bath temperature a mechanical heat switch was used. The powdered salts were pressed into a thin walled gold-plated finned copper calorimeter to improve internal heat contact [9].

The paramagnetic susceptibility was measured by means of a PAR vibrating sample magnetometer, model 150, in the 2—80 K region at fields around 5000 Oersted.

Results and Discussion

From the methods avaialable for determining large D-values (viz. single-crystal EPR spectra, heat capacity measurements, single-crystal magnetic anisotropies, paramagnetic powder susceptibilities, and direct spectroscopic measurements), we have chosen the heat capacity and powder paramagnetic susceptibility at low temperatures, as single crystals of the compounds of sufficiently large size were not available and far-infrared and Raman spectra were expected to be disturbed by interaction with lattice vibrations.

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