Journal of Atmospheric and Terrestrial Physics, 1972, Vol. 34, pp. 787 to 794. Pergamon Press. Printed in Northern Ireland

Electron–ion and ion–ion reaction rate coefficients at low altitudes during a PCA event

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(*Received* 4 *October* 1971)

Abstract—Based on experimental data from several ESRO PCA rocket flights some considerations are presented regarding the mean values of the electron–ion dissociative recombination coefficient (α_d) and the ion–ion neutralization coefficient (α_i). The estimates yield values for $\alpha_d = 10^{-5}$ cm^3 sec^{-1} for heights between 60 and 67 km. The data indicate that α_i is smaller than α_d by a factor of 100.

1. INTRODUCTION

THIS paper is concerned with chemical reaction rates in the lower *D*-region (60–67 km) during a polar cap absorption (PCA) event.

By combining the results of simultaneous *in situ* rocket measurements of ionizing particle energy spectra and ambient electron and positive ion densities both during day and night time conditions the possibility of estimating a mean value for the electron–ion recombination rate (α_d) and of setting an upper limit on the ion–ion neutralization rate (α_i) is demonstrated.

In Section 2 some background material will be mentioned and the relevant theoretical expression developed. The experiments on which this paper is based are described in Section 3. The ion-pair production is discussed in Section 4 and the observational results are presented and evaluated in Section 5. Some remarks on the uncertainties involved are given in Section 6.

2. THEORY

The positive-ion-mass spectrometer experiments by NARCISI and BAILEY (1965) showed that the dominating positive ion below 82 km had mass 37^+. In addition to the expected molecular species NO^+ (mass 30) and O_2^+ (mass 32) an ion with mass 19^+ was found. The ion 19^+ and 37^+ are thought to be water cluster ions of type $H_3O^+ \cdot (H_2O)_n$, where $n = 0$ and 1. In recent years the dynamic range of the ion mass spectrometers has been extended to larger masses, and hydrated ions with $n \geq 2$ have also repeatedly been observed (see e.g. KRANKOWSKY *et al.*, 1971). The presence of such ions will influence our thinking regarding *D*-region chemical reactions and reaction coefficients.

Recent measurements by BIONDI (private communication, 1971) of electron–water ions recombination coefficients give values that are increasing from $1 \cdot 3 \times 10^{-6}$ cm^3 sec^{-1} for 19^+ to $4 \cdot 6 \times 10^{-6}$ cm^3 sec^{-1} for 55^+ at a temperature of 300°K. At mesospheric temperatures (~180°K) these reaction coefficients are expected to be even higher. Such reaction coefficients are much higher than the value 4×10^{-7} cm^3 sec^{-1} for NO^+ determined by YOUNG and ST JOHN (1966). Other published values for O_2^+ and NO^+ range between about 10^{-6} and 10^{-7} cm^3 sec^{-1} (BIONDI, 1969). In an attempt to explain the steep ledge in electron density typically observed at altitudes 80–90 km, REID (1970) inferred recombination coefficients for undisturbed conditions that vary from about 6×10^{-7} cm^3 sec^{-1} at 90 km, to 5×10^{-5} at 85 km and 2×10^{-5} cm^3 sec^{-1} at 70 km. Recently, a two-ion model for the D-region has been developed (HAUG and LANDMARK, 1970). One ion species has an electron–ion dissociative recombination coefficient (α_d) much smaller than the second ion species, which is assumed to be some sort of cluster ion with α_d equal to 10^{-4} cm^3 sec^{-1} or greater. The production of the cluster ion is assumed to be proportional to the density of the more slowly recombining ion. In the height region of approx 70–80 km, this theory predicts that the production (q) of ion pairs is proportional to the electron density N rather than to N^2 as normally assumed. During polar cap and auroral absorption events with large electron densities, the main part of the loss of ionization may not necessarily be through processes involving the rapidly recombining ions (HAUG and LANDMARK, 1970). However, FOLKESTAD and ARMSTRONG (1970) are able successfully to explain rocket observations in the altitude range 70–78 km during auroral conditions in terms of the two-ion theory described above. The observed electron loss rates were too large to allow an interpretation using classical electron–ion and ion–ion recombination coefficients. There are indications (BROWN, 1970) that very disturbed conditions, at least above 80 km, favour the formation of intermediate ion species at the expense of water cluster ions further along the chain.

It is our purpose to show that even during a polar cap absorption event (PCA) values for α_d of the order 10^{-5} cm^3 sec^{-1} are inferred at low ionospheric levels (60–70 km). Before the experimental data are presented, we shall give the relation between ion-pair production (q) and electron density (N), which for steady state conditions is usually written as:

$$q = (1 + \lambda)(\alpha_d + \lambda\alpha_i)\, N^2$$

where $\lambda = N^-/N$, N^- being negative ion density, while α_d and α_i are the electron–positive ion dissociation recombination coefficient and ion–ion neutralization coefficient respectively. Using the charge neutrality relation $N^+ = N^- + N$ equation (1) may be written:

$$q = (\alpha_d + \lambda\alpha_i)N^+N \tag{2a}$$

or

$$\frac{q}{NN^+} = (\alpha_d + \lambda\alpha_i). \tag{2b}$$

We now claim that an altitude plot of the entity $q/N \,.\, N^+$ should reveal interesting clues for determining dominant D-region loss processes. If the term $\lambda\alpha_i$ is important, ($\lambda\alpha_i > \alpha_d$), one expects to see a λ-variation in an altitude plot of $q/N \,.\, N^+$ as λ is found to increase with decreasing altitude (see e.g. MITRA, 1968). One would also expect to see a change in this entity in going from day to night conditions, as λ in the height region which we will consider, 60–70 km, is measured to be much larger (typically a factor of 10^2) during night-time. On the other hand if such variations are not found, one would be led to assume that electron–ion recombination is the more important loss process in this height region, that is $\alpha_d \gg \lambda\alpha_i$. The magnitude of $q/N . N^+$ should indicate whether or not recombination is through very fast recombining ions, as suggested by Haug and Landmark.

3. Experimental Data

All the experimental data were collected in an ESRO campaign, during which four instrumented rocket were flown, in the course of the first 15 hr of a PCA, from Andöya Rocket Range, North Norway (geomagnetic latitude 67° N, $L = 6{\cdot}2$). The PCA started following a sudden ionospheric disturbance event at 0911 UT on 25 February 1969 and was of moderate strength (123 on the PCA-index scale suggested by Smart and Shea, 1970).

The experimental data are D-region electron density height profiles measured by Jespersen *et al.* (1970), positive ion density profiles determined by Murdin and Bowling (1970) and energy spectra of precipitating protons measured by Van Beek and Stevens (1970). The electron density height profile is determined by the Faraday rotation and differential absorption techniques at three frequencies 3·8, 7·8 and 15·0 MHz. The positive ion density is derived from the current of a cylindrical electrostatic probe. The precipitating proton fluxes were measured in four energy ranges viz. 2·3–5·5, 5·5–13, 13–30 and 30–70 MeV by a solid-state detector. The detector was mounted so as to cover all pitch angles when the rocket was spinning. For further information concerning these experiments the reader should consult the references given above.

We will use data from a daytime rocket (A40/3) and a night-time rocket (A40/4) launched at 1421 and 2137 UT, respectively, on 25 February 1969. The latter rocket reached an altitude of only 67 km, and we must therefore limit our discussion of the night-time conditions to heights below this altitude. The rocket measurements from A40/3 and A40/4 give day and night values of N and N^+ as a function of altitude. These data are shown in Fig. 1. Figure 2(a) gives the proton differential energy spectrum measured on board A40/3. The data are fitted to a power law of the form $dN/dE = N_0E^{-\gamma}$, where N_0 is the particle flux at a reference energy (here 1 MeV) and E is the particle energy. The exponent γ determines the spectral hardness. The particle data cover the energy range of about 1–100 MeV, but for the heights we are considering particles with energies between 5–10 MeV are most important in the ion-pair production.

For the day-time shot A40/3 we thus have *simultaneously* recorded data which enables us to compute $q/N . N^+$ as a function of height. For the night-time rocket A40/4 direct measurements of the precipitating particles do not exist as an instrument protective belt on the rocket did not release. However, spectra were obtained from two other rocket flights, C I and C II, one before and the other after the A40/4 flight, the launching times for these rockets are 1633 and 2350 UT (see Fig. 2(b) and (d)).

These differential energy spectra of precipitating protons (Figs. 2(a, b and d)) were then corrected for atmospheric absorption to yield the incident particle spectrum on the top of the atmosphere. Using the resulting spectra a linear interpolation was

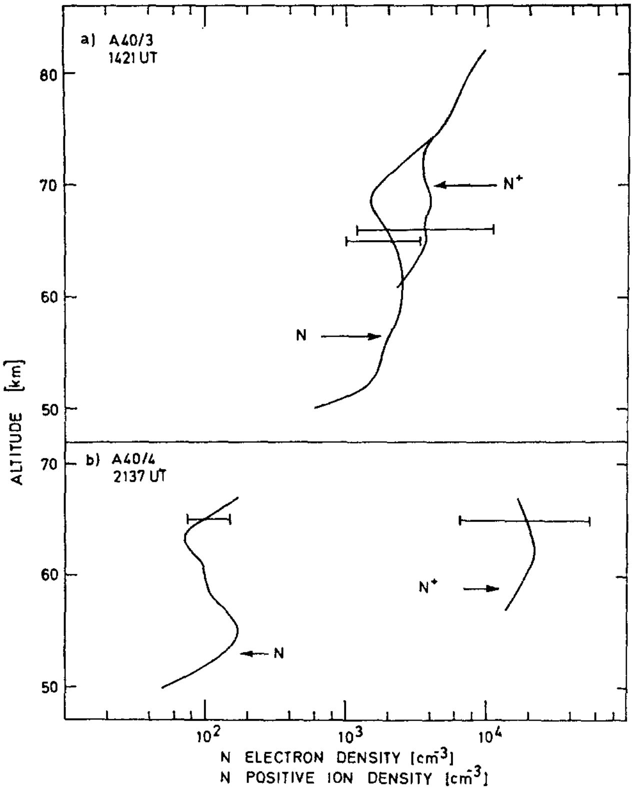

Fig. 1. Electron density (N) and positive ion density (N^+) altitude profiles for two rocket shots, A40/3 and A40/4 launched from Andenes on 25 February 1969 (for references see text).

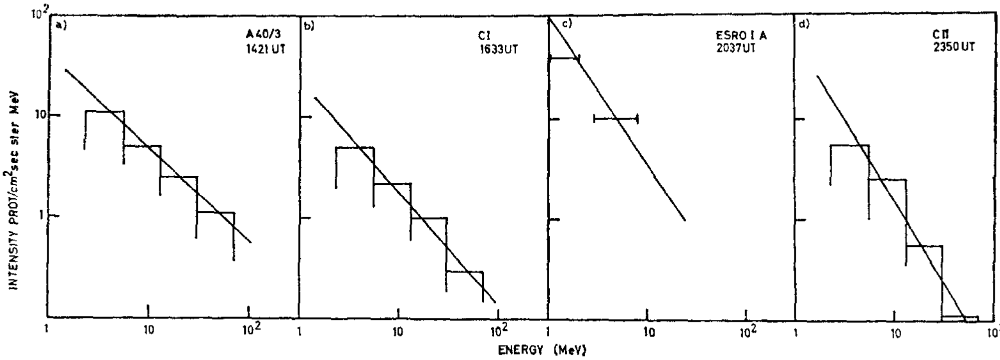

Fig. 2(a, b and d). Uncorrected energy spectra of precipitating protons measured by rockets launched from Andenes on 25 February 1969 (Van Beek and Stevens, 1970).

Fig. 2(c). Energy spectrum of precipitating protons measured by the ESRO I A satellite on 25 February 1969 (Söraas, private communication).

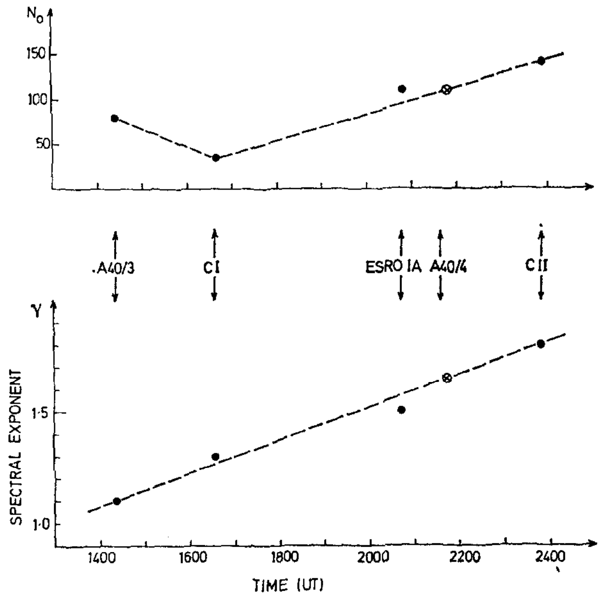

Fig. 3. Spectral parameters (N_0 and γ) of corrected proton energy spectra. Also shown are the values assumed for the spectrum at 2137 UT (time of A40/4 flight).

made to find N_0 and γ-values representative for the time 2137 UT (time of A40/4 launch). Figure 3 shows that the γ-values seem to increase consistently during the period considered here (indicating a softening of the particle spectrum) while the N_0 values vary somewhat differently. The figure also indicates the N_0 and γ-values assumed for the A40/4 flight. This method of determining the particle spectrum may of course be questioned, but we believe in the deduced spectrum for two reasons:

(a) The particle fluxes (in the MeV range) and the spectrum hardness changed rather slowly at this stage of the PCA event (Söraas *et al.*, 1970).

(b) A proton spectrum, (shown in Fig. 2(c)), determined from ESRO I A satellite data (Söraas, private communication) at 2049 UT at appropriate L-values, but some 50° longitude west of the Andöya Rocket Range is essentially identical with the spectrum we have deduced for the A40/4 flight at 2137 UT (see Fig. 3).

This rather lengthy description of the particle data we feel is necessary in order to spell out all our assumptions.

4. Ion-Pair Production

The ion-pair production in the lower ionosphere resulting from the precipitating protons is computed using a program developed at NDRE. Isotropic particle fluxes are assumed (well documented by the experimental data) and proton energies between 1 and 100 MeV are considered. The program is based on a formulation presented by Maeda (1963). Charge transfer and backscatter are not included.

5. RESULTS AND DISCUSSION

We present in Fig. 4 plot of the computed effective recombination rate $\alpha_{eff} = q/N^2 = (1 + \lambda)(\alpha_d + \lambda\alpha_i)$ as a function of altitude for the day and night shot. Note that in the region 60–67 km the α_{eff} values are 100–200 times larger at night-time than during day-time.

The observed, large change in α_{eff} from 2×10^{-7} at 82 km to about 2×10^{-5} $cm^3 sec^{-1}$ at 70 km for the daytime shot probably reflects the transition from a region where NO^+-ions dominate to a region where hydrated ions dominate. During quiet ionospheric conditions such a change takes place somewhat higher up (between 80 and 90 km), and we conjecture that the high electron density concentration present during PCA conditions effectively prevents the formation of hydrated ions above about 70–75 km.

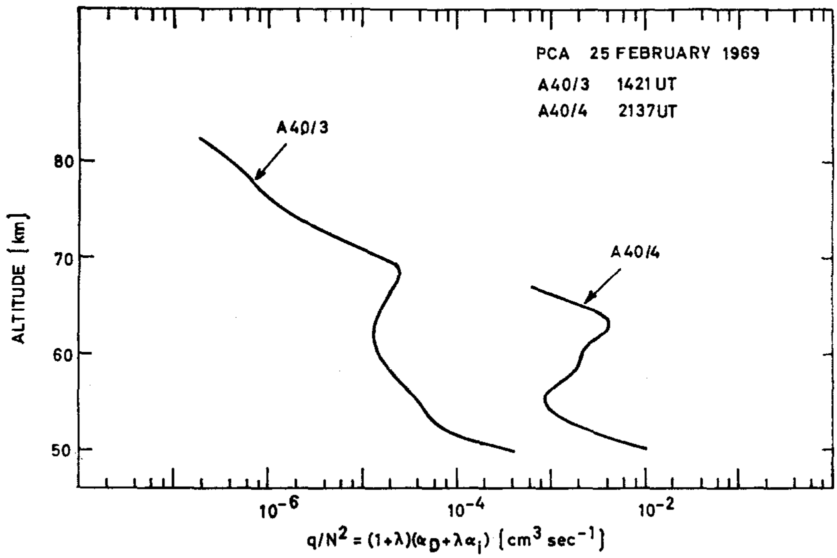

Fig. 4. Effective recombination coefficient $q/N^2 = \alpha_{eff}$ as a function of altitude for the flights A40/3 and A40/4.

Furthermore, based on the described measurements of N and N^+ and the computed q-values the expression $q/N \,.\, N^+ = (\alpha_d + \lambda\alpha_i)$ is evaluated at different ionospheric heights. The results are shown in Fig. 5. In addition to the curves obtained by using only the rocket data, a q/NN^+-plot using the ESRO I A proton spectrum as ionizing source instead of the deduced A40/4 spectrum is given. The horizontal lines joining the night-time values thus indicate roughly the uncertainty in q/NN^+ due to insufficient knowledge of the precipitating particle spectrum.

We see from Fig. 5 that in the region between about 60 and 67 km, the expression $q/NN^+ = (\alpha_d + \lambda\alpha_i)$ is rather height independent with a value of the order 10^{-5} $cm^3 sec^{-1}$ both for day and night conditions. From Fig. 1 we deduce that λ is of the order 1 and 100 for day and night, respectively, in this height range (remember that $\lambda = N^-/N = (N^+/N) - 1$). Assuming that no significant chemical changes at these ionospheric levels take place in the time between the two rocket shots, i.e. constant α_d and α_i, we thus conclude that $\alpha_d \gg \lambda\alpha_i$ even at night.

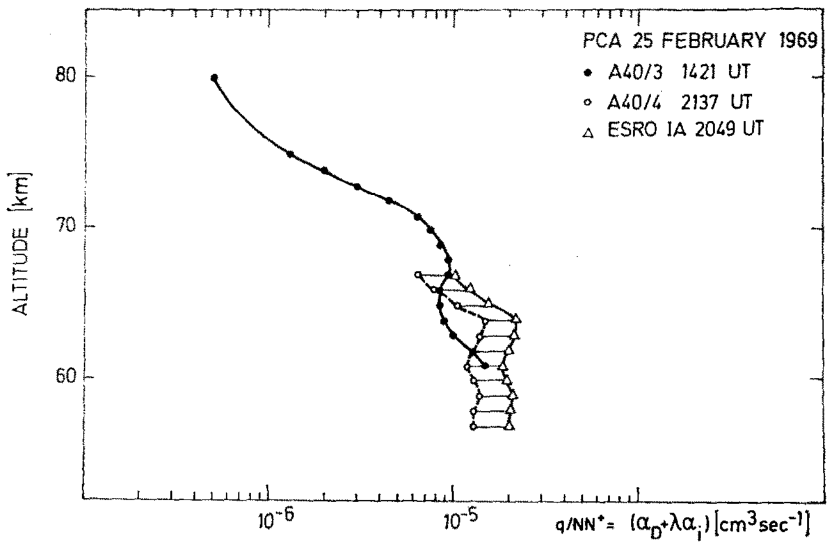

Fig. 5. Altitude plot of $q/NN^+ = (\alpha_d + \lambda\alpha_i)$ for the flights A40/3 and A40/4 (circles). The curve marked by triangles is deduced by using the ionization values calculated using the ESRO I A proton spectrum and the N and N^+ measurements on A40/4. Notice that the day and night values of $q/NN^+ = (\alpha_d + \lambda\alpha_i)$ are approximately equal.

Therefore, the dominating electron loss process between 60 and 67 km seems to be dissociative recombination with positive ions with a reaction coefficient of the order 10^{-5} cm^3 sec^{-1}.

The derived value of about 10^{-5} cm^3 sec^{-1} for α_d is much larger than the rate usually assigned to electron dissociative recombination with NO^+ (typically 10^{-6}–10^{-7} cm^3 sec^{-1}).

An upper limit to α_i can be set by noting that $\alpha_d = 10^{-5}$ cm^3 sec$^{-1} \gg 100 \cdot \alpha_i$, where the night-time value of λ has been used. Thus: $\alpha_i \leqslant 10^{-7}$ cm^3 sec^{-1}. It is interesting to compare this value with laboratory data for α_i which range from 10^{-7} to 10^{-8} cm^3 sec^{-1} (Biondi, 1969).

6. Discussion of Uncertainties

The measurements and computations on which this note is based, are inherently affected by uncertainties, which, however, are difficult to assess in terms of error bars on the points in Fig. 5. We shall, however, indicate the order of magnitude of the uncertainties involved. Murdin and Bowling (1970) argue that the N^+ values may be wrong by a factor of 3 due to uncertainties in the magnitude of the probe to plasma voltage and the ion mobility. The electron density profile is probably more accurately determined than the N^+ profile. It is reasonable to assume that the densities given may be wrong by a factor of 1·5, probably less. The uncertainty in q is due to uncertainties in the knowledge of the precipitating proton spectrum and in the assumptions and procedure by which the ion-pair production is calculated. We feel that the q's may be uncertain by a factor of 3 or less.

With these rather radical estimates of the uncertainties involved we end up with a relative uncertainty in q/NN^+, or as we have tried to show, in α_d, of a factor 5. Taking this factor into consideration, however, we still end up with α_d values larger than 2×10^{-6} cm^3 sec^{-1}.

In conclusion we therefore argue that the given experimental data lead us to believe that the main electron loss in the 60–67 km region at day and night is through a fast recombination process with an effective reaction rate of the order 10^{-5} cm^3 sec^{-1}. We stress that this value is our best estimate from the given material but it should not be used uncritically.

Acknowledgement—The data used above were collected during an ESRO PCA rocket campaign from Andenes, Norway. Mr T. JACOBSEN has developed the computer program for ion-pair production and his assistance is greatly appreciated.

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