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**Abstract**

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*GEOPHYSICS*

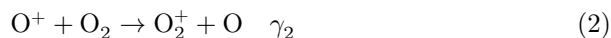
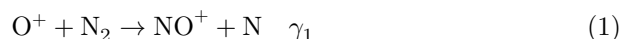
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**RATES OF THE PRINCIPAL ION-MOLECULAR PROCESSES IN THE IONOSPHERE**

*(Presented by Academician E. K. Fedorov, 29 X 1965)*

The determination of rate constants for ionization-recombination processes in the upper atmosphere encounters well-known difficulties. As follows from the review paper <sup>(1)</sup>, the scatter in the data of laboratory investigations of the constants of the principal reactions is very large and does not allow reliable values to be chosen for ionospheric studies. Quite recently, several works have appeared on the investigation of ion-molecular reactions in the ionosphere and in the laboratory which require discussion in order to select the most reliable values of the constants.

Table 1 gives the results of a laboratory investigation of two principal ionospheric ion-molecular reactions



As can be seen from this table, even if one discards the high value  $2 \cdot 10^{-10} \text{ cm}^3 \text{ sec}^{-1}$  given by Paulson (since it contradicts the estimate  $\gamma_1 \leq 5 \cdot 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$  given in his own review paper <sup>(9)</sup>), as well as the high value  $\gamma_1 \approx 10^{-8} \text{ cm}^3 \text{ sec}^{-1}$ , which, as has already been noted more than once, is probably erroneous, there remains a scatter of the most reliable of the obtained values of the rate constant of reaction (1) by an order of magnitude, with both the high and the low value being confirmed by two experiments. A somewhat better situation is observed for the constant of reaction (2), but here too one must reject the result of experiment <sup>(5)</sup>, which (as we shall see below) gives the value of  $\gamma_1$  most acceptable from the point of view of ionospheric studies, so that the remaining values of  $\gamma_2$  can be reconciled with one another to within a factor of 2.

**Table 1**

| No. | Author   | $\gamma_1$                | $\gamma_2$              |
|-----|--|---------------------------|-------------------------|
| 1   | Potter <sup>(2)</sup>                            | $10^{-8}$                 | —                       |
| 2   | Dickinson and Sayers <sup>(3)</sup>              | —                         | $2.5 \cdot 10^{-11}$    |
| 3   | Tal' roze et al. <sup>(4)</sup>                  | $\leq 6.7 \cdot 10^{-11}$ | —                       |
| 4   | Langstroth and Hasted <sup>(5)</sup>             | $4.7 \cdot 10^{-12}$      | $1.8 \cdot 10^{-12}$    |
| 5   | Fayt et al. <sup>(6)</sup>                       | —                         | $(1-10) \cdot 10^{-11}$ |
| 6   | Wolley et al. <sup>(7)</sup>                     | $2.2 \cdot 10^{-11}$      | —                       |
| 7   | Sayers and Smith <sup>(8)</sup>                  | $2.7 \cdot 10^{-11}$      | $1.6 \cdot 10^{-11}$    |
| 8   | Paulson and Moser (according to <sup>(9)</sup> ) | $\leq 5 \cdot 10^{-11}$   | —                       |
| 9   | Paulson et al. <sup>(10)</sup>                   | $2 \cdot 10^{-10}$        | —                       |
| 10  | Fesenfeld et al. <sup>(11, 12)</sup>             | $3 \cdot 10^{-12}$        | $4 \cdot 10^{-11}$      |

*Reaction constants (1) and (2), cm<sup>3</sup> sec<sup>-1</sup>*

Table 2 gives estimates of the efficiency of the same processes (1) and (2), obtained by different authors on the basis of analysis of ionospheric data. It should be noted that in obtaining the estimates given in Table 2, different authors used various initial data, such as, for example: altitude measurements of the ionic composition in the 100-200 km region <sup>(16)</sup>, altitude and diurnal variations of ion concentrations <sup>(17)</sup>, measurements of the linear recombination coefficient in the  $F_2$  region <sup>(19)</sup>, etc. To obtain the estimates given in the 8th row of Table 2, relations between the constants of ion-molecular reac-

and dissociative recombination <sup>(24-26)</sup>  $\gamma_1/\alpha_{\text{NO}^+}^* = (5-10) \cdot 10^{-5}$ ,  $\gamma_2/\alpha_{\text{O}_2^+}^* = (1-2) \cdot 10^{-4}$ . The quantities  $\alpha_{\text{NO}^+}^*$  and  $\alpha_{\text{O}_2^+}^*$ , which have been studied in the laboratory more reliably than the constants  $\gamma_1$  and  $\gamma_2$ , were taken from the review work <sup>(21)</sup> for a temperature of about 1000° K. Thus, the estimates of  $\gamma_1$  and  $\gamma_2$  given also refer to the indicated temperature.

From the data considered in Table 2 it is seen that the ionospheric estimates of different authors generally do not differ greatly from one another, leading to mean values of the constants of processes (1) and (2)  $\gamma_1 = 2 \cdot 10^{-12}$  cm<sup>3</sup> · sec<sup>-1</sup>,  $\gamma_2 = 2 \cdot 10^{-11}$  cm<sup>3</sup> · sec<sup>-1</sup>, and these mean values of  $\gamma$  differ by no more than a factor of 2-3 from the most reliable estimates given in rows 3-9 of Table 2. The

values of  $\gamma$  obtained in works (<sup>14,15</sup>) should be regarded as underestimated. They agree neither with the most reliable ionospheric estimates nor with laboratory data.

**Table 2**

| No. | Author   | Constants of reactions (1) and (2), $\text{cm}^3 \text{sec}^{-1}$ | Constants of reactions (1) and (2), $\text{cm}^3 \text{sec}^{-1}$ |
|-----|--|---|---|
| No. | Author   | $\gamma_1$  | $\gamma_2$  |
| 1   | Bates and Nicolet ( <sup>14</sup> )                                    | $\gamma_1 + 0.16\gamma_2 = 1.3 \cdot 10^{-13}$                    |   |
| 2   | Khartak and Rivi ( <sup>15</sup> )                                     | $\ll 10^{-13}$  | $\ll 10^{-12}$  |
| 3   | Norton et al. ( <sup>16</sup> )  | $1 \cdot 10^{-12}$  | $5 \cdot 10^{-11}$  |
| 4   | Danilov ( <sup>17</sup> )  | $(0.5-1) \cdot 10^{-12}$  | $(0.5-1) \cdot 10^{-11}$  |
| 5   | Whitten and Popoff ( <sup>18</sup> )                                   | $2 \cdot 10^{-12}$  | $2 \cdot 10^{-11}$  |
| 6   | Nisbet and Quinn ( <sup>19</sup> )                                     | $\leq 1.3 \cdot 10^{-12}$   | $\leq 10^{-11}$   |
| 7   | Sagalin and Smiddy ( <sup>20</sup> )                                   | $(1.6-3.2) \cdot 10^{-12}$  |   |
| 8   | Danilov (from $\gamma/\alpha^*$ and $\alpha^*$ from ( <sup>21</sup> )) | $(1.5-3) \cdot 10^{-12}$  | $(0.6-1.1) \cdot 10^{-11}$  |
| 9   | Holl et al. ( <sup>22</sup> )  | $\gamma_1 + 0.12\gamma_2 \simeq 3 \cdot 10^{-12}$                 |   |
| 10  | Danilov and Yatsenko ( <sup>23</sup> )                                 | $\gamma_1/\gamma_2 \approx 0.1$                                   |   |

As for the laboratory data, the values of  $\gamma_1$  and  $\gamma_2$  obtained from ionospheric data allow one to assert that the values of  $\gamma_1$  found in works (<sup>5,11</sup>) are correct, while those obtained in the experiments (<sup>7,8</sup>) are overestimated.

In an analogous way it should be accepted that the value  $\gamma_2 = 1.8 \cdot 10^{-12} \text{ cm}^3 \cdot \text{sec}^{-1}$  is greatly underestimated, while the value  $\gamma_2 = 4 \cdot 10^{-11} \text{ cm}^3 \cdot \text{sec}^{-1}$  obtained in recent experiments (<sup>12</sup>) is somewhat overestimated. The obtained estimates of the constants of the main ion-molecular reactions in the ionosphere appear sufficiently reliable (in any case, within a factor of 2). Some uncertainty is introduced only by the temperature dependence of the constants  $\gamma_1$  and  $\gamma_2$ . According to experiments (<sup>8</sup>), the constant of reaction (2) depends on temperature as  $T^{-1}$  in the region  $210^\circ \leq T \leq 452^\circ \text{ K}$ . From theoretical considerations, dependences of the constants of ion-molecular reactions on temperature generally should not be observed (<sup>9,27,28</sup>). According

to (13), in the experiments of Giese and Stebbings a direct dependence between  $\gamma_1$  and  $T$  was obtained at energies of several electron volts. Thus, the question of the temperature dependence of the constants requires further experimental investigation.

**Table 3**

| Reactions                                 | Freit et al. (8) | Wolpin et al. (7)       | Paulson et al. (10) | Ferguson et al. (11-13) | Khartak (29) |
|---|------------------|-------------------------|---------------------|-------------------------|--------------|
| (3) $N^+ + O_2 \rightarrow NO^+ + O$      |                  | $1 \cdot 10^{-10}$      | $3 \cdot 10^{-10}$  | $5 \cdot 10^{-10}$      | $10^{-16}$   |
| (4) $O_2^+ + N_2 \rightarrow NO^+ + NO$   |                  | $\ll 2 \cdot 10^{-13}$  | $4 \cdot 10^{-11}$  | $< 10^{-15}$            | —            |
| (5) $N_2^+ + O_2 \rightarrow NO^+ + NO$   |                  | $\leq 2 \cdot 10^{-13}$ | $4 \cdot 10^{-11}$  | —                       | —            |
| (6) $N_2^+ + O_2 \rightarrow O_2^+ + N_2$ |                  | —                       | —                   | $1.0 \cdot 10^{-10}$    | —            |
| (7) $N_2^+ + O \rightarrow NO^+ + N$      |                  | —                       | —                   | $2.5 \cdot 10^{-10}$    | —            |
| (8) $N_2^+ + O \rightarrow N_2 + O^+$     |                  | —                       | —                   | $< 10^{-11}$            | —            |
| (9) $N^+ + O_2 \rightarrow O_2^+ + N$     |                  | —                       | —                   | $(0.5-1) \cdot 10^{-9}$ | —            |

Table 3 gives the results of laboratory measurements of the constants of ion-molecular reactions in which the main constituents of the atmosphere take part: O, O<sub>2</sub>, and N<sub>2</sub>. Most of these reactions were studied in works (11-13). As in Table 1, here the values obtained by Paulson attract attention; they differ sharply from the data of other authors, which forces one to suppose that Paulson's experiment (10) is erroneous. Ionospheric estimates of the constants of these reactions are more-

less complex than the principal reactions (1) and (2). It should be noted that the value  $\gamma_7 \approx 1.0 \cdot 10^{-11}$  obtained in (16), and  $\gamma_7 \approx 2 \cdot 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$  obtained in (18), as well as the estimate  $\gamma_4 = (3-10) \cdot 10^{-14} \text{ cm}^3 \text{ sec}^{-1}$ , made in (26) on the basis of an analysis of data on the ionic composition in the region 100-150 km.

**Table 4**

| Reactions                                | Value of $\gamma$ according to (13) |
|--|-------------------------------------|
| $O^+ + NO \rightarrow NO^+ + O$ (10)     | $(2.4 \pm 1) \cdot 10^{-11}$        |
| $N_2^+ + NO \rightarrow NO^+ + N_2$ (11) | $5 \cdot 10^{-10}$                  |
| $O_2^+ + NO \rightarrow NO^+ + O_2$ (12) | $8 \cdot 10^{-10}$                  |

| Reactions                             | Value of $\gamma$ according to (13) |
|---------------------------------------|-------------------------------------|
| $O_2^+ + N \rightarrow NO^+ + O$ (13) | $(1.8 \pm 0.5) \cdot 10^{-10}$      |
| $N^+ + NO \rightarrow NO^+ + N$ (14)  | $(8 \pm 1) \cdot 10^{-10}$          |

Table 4 gives the results of laboratory experiments on the study of the constants of ion-molecular processes involving minor atmospheric constituents—neutral NO molecules and nitrogen atoms.

As is seen from this table, the constants obtained in the laboratory are very high; therefore the view that prevailed until recently, namely that the indicated reactions could be neglected because of the low concentrations of NO and N, must be reconsidered. The exact values of these concentrations are still unknown to us; however, the high values of the constants require a detailed analysis of these processes when considering equilibrium ion concentrations, especially in the region 100–130 km.

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*Note: Figure translations are in progress. See original paper for figures.*

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