

### 911. *The Photochemical Decomposition of Rubidium and Cæsium Azides.*

By P. W. M. JACOBS and A. R. TARIQ KUREISHY.

Rubidium azide resembles potassium azide in that the rate of photolysis at first decreases, passes through a minimum and then increases, finally attaining a constant value. The rate of photolysis of cæsium azide decreases, becomes constant for a brief period and then decreases again before becoming constant. It is shown that the overall rate curves for these reactions can result from the superposition of three curves, one for each reaction mechanism; two of these processes have been described previously. The third is considered to involve the reaction of excitons and excited azide ions at metal nuclei and to produce  $N_4^-$  ions. The subsequent thermal decomposition of these ions is responsible for the dark reaction that occurs on switching off the lamp. A photochemical reaction between nitrogen gas and rubidium metal has been noted.

THE photolysis of sodium, potassium, strontium, and barium azides has previously been studied by Jacobs, Tompkins and co-workers.<sup>1-11</sup> When these salts are irradiated by the

<sup>1</sup> Thomas and Tompkins, *Proc. Roy. Soc.*, 1951, *A*, **209**, 550.

<sup>2</sup> Thomas and Tompkins, *Proc. Roy. Soc.*, 1951, *A*, **210**, 111.

<sup>3</sup> Thomas and Tompkins, *J. Chem. Phys.*, 1952, **20**, 662.

<sup>4</sup> Jacobs and Tompkins, *Proc. Roy. Soc.*, 1952, *A*, **215**, 254.

<sup>5</sup> Jacobs and Tompkins, *Proc. Roy. Soc.*, 1952, *A*, **215**, 265.

<sup>6</sup> Tompkins and Young, *Discuss. Faraday Soc.*, 1957, **23**, 202.

<sup>7</sup> Jacobs, Tompkins, and Young, *Discuss. Faraday Soc.*, 1959, **28**, 234.

<sup>8</sup> Cunningham, unpublished work.

<sup>9</sup> Jacobs, Tompkins, and Pai Verneker, *J. Phys. Chem.*, 1962, **66**, 1113.

<sup>10</sup> Jacobs, Sheppard, and Tompkins, to be published.

<sup>11</sup> Jacobs and Kureishy, to be published.

ultraviolet light from a low pressure (L.P.) mercury lamp, the rate of photolysis decreases initially. For the sodium salt, the rate becomes constant after an initial decay but, for the other azides investigated, it rises after passing through a minimum value, eventually becoming constant. If the radiation from the L.P. lamp is filtered through a water filter to remove radiation of wavelength shorter than 2000 Å, the accelerative process in potassium, strontium and barium azides is not observed. It has been suggested<sup>9-10</sup> that this process is associated with the metal produced during the initial decelerative reaction. The photochemical decomposition of rubidium and caesium azides has not been studied previously, although some information on colour-centre formation in these salts due to X-ray<sup>12</sup> and ultraviolet<sup>13</sup> irradiation is available.

#### EXPERIMENTAL

The photolysis reaction was studied by using a Pirani gauge to measure the pressure of nitrogen gas evolved in a constant volume system. The initial pressure before starting a run was  $<10^{-6}$  mm. of mercury and the outgassing rate of the order of  $10^{-5}$  mm./hr. The sample was spread uniformly at the bottom of a silica cell. The source of radiation was a L.P. mercury lamp with strong emission at 2537 Å and a number of weaker components of longer and shorter wavelengths. The full spectrum of this source has been described elsewhere;<sup>7</sup> an important component below 2000 Å is the 1849 Å line. The intensity of irradiation was varied by changing the current in the primary circuit of the power supply to the lamp, which was calibrated with a Kipp thermopile. The salts used in this study were kindly supplied by the Ministry of Aviation E.R.D.E. at Waltham Abbey. They were subsequently stored in a desiccator over phosphorus pentoxide for a prolonged period.

#### RESULTS AND DISCUSSION

*Rubidium Azide.*—Fig. 1A shows the rate of photolysis *vs.* the number of nitrogen molecules evolved for a 200 mg. sample of rubidium azide at the temperature of solid carbon dioxide.\* The rate falls initially, reaches a minimum value and then rises, finally becoming constant. After a total irradiation time of 258 min. at an intensity of  $1.79 \times 10^{15}$  quanta  $\text{cm.}^{-2} \text{sec.}^{-1}$ , the lamp was switched off and the sample warmed up to ice temperature. (Again, this will be referred to as 0°, although the actual salt temperature with the reaction vessel immersed in ice + water is about 2°.) The dark rate,  $R_d$ , increases to a very high value and then decreases steadily after the sample has attained a constant temperature. The plot of  $R_d^{\frac{1}{2}}$  against  $N_d$  the number of nitrogen molecules evolved during the dark reaction is shown in Fig. 2A, the dotted line showing the warm-up period. The ratio of the total gas evolved in the dark reaction and the photolysis reaction  $g_d/g_l$  is 1.6. The sample was then left open to the pumps for 20 hours at room temperature and photolysed at this temperature (22°). The plot of rate against the number of nitrogen molecules evolved is shown in Fig. 1B (Curve a). The rate rises sharply to a stable value, stays constant for a period and starts to rise again, finally becoming constant; curve b of the same figure shows the decay of the dark rate. Curves c and d show the result of a similar experiment at 0°. During the dark reaction, if the sample is opened to pumps the dark rate increases (Fig. 1B, Curve e), but its decelerative character remains unchanged. The linear plots of  $R_d^{\frac{1}{2}}$  against  $N_d$  for these runs are shown in Fig. 2B. The ratio  $g_d/g_l$  is 0.24 at room temperature. The results obtained with rubidium azide powder were quite reproducible qualitatively, but not quantitatively. An attempt to obtain better reproducibility by depositing a thin film of rubidium azide was unsuccessful. The film was deposited by freeze-drying a hydrazoic acid solution containing 60 mg. of rubidium azide. The photolysis rate for this film was about three times as high as that obtained

\* For brevity, this temperature will subsequently be referred to as  $-80^\circ$ , although it must be appreciated that the figure is nominal. With the reaction cell immersed in solid carbon dioxide + acetone, the salt temperature rises under irradiation to above  $-80^\circ$ . The extent of this rise is uncertain but unimportant, because little quantitative use is made of the reaction temperature.

<sup>12</sup> Heal and Pringle, *J. Phys. and Chem. Solids*, 1960, **15**, 261.

<sup>13</sup> Papazian, *J. Phys. and Chem. Solids*, 1961, **21**, 81.

from 200 mg. of powder. The colour of the film changed to violet when it was irradiated at  $-80^\circ$  and this colour disappeared when the film was warmed up to  $0^\circ$ .

When a fresh sample of rubidium azide is irradiated through a water filter, the rate of photolysis increases slightly in the beginning and then decays slowly (Fig. 3a); the accelerative process observed without a water filter is absent. The dark rate diminishes very quickly to a negligible value. If the sample is left in contact with nitrogen for 16 hours and the sample is photolysed again through a water filter, the pressure in the system

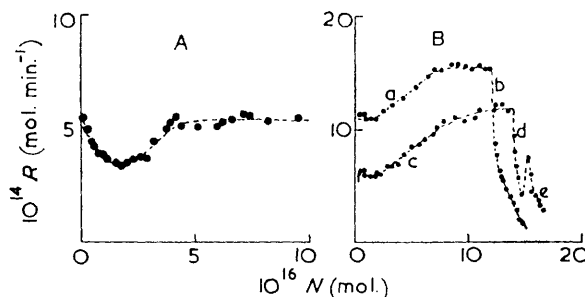


FIG. 1. Rate of photolysis of rubidium azide as a function of  $N$ , the number of nitrogen molecules produced in the reaction.

- A. Fresh azide at  $-80^\circ$ ,  $I = 1.79 \times 10^{15}$  quanta  $\text{cm}^{-2} \text{sec}^{-1}$ .  
 B. Previously decomposed rubidium azide conditioned at room temperature *in vacuo*.  
 (a) Photolysis at  $22^\circ$ . (b) Dark rate at  $22^\circ$ . (c) Photolysis at  $0^\circ$ . (d) Dark rate at  $0^\circ$ . (e) Dark rate at  $0^\circ$  after pumping off nitrogen.

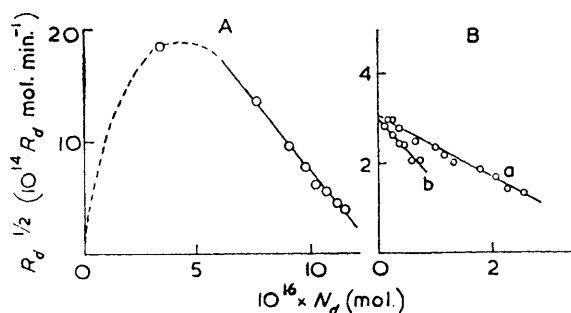


FIG. 2. Square root dependence of the dark rate,  $R_d$ , on  $N_d$ , the number of molecules produced in the dark reaction, illustrating second order kinetics.

- A. On warming up the sample to  $0^\circ$  after it had previously been decomposed photochemically at  $-80^\circ$ ; the dotted line shows the warm-up period.  
 B. Second-order plots for the dark reaction at (a)  $22^\circ$  and (b)  $0^\circ$ .

decreases, giving a negative rate, which rises with time to a constant positive value (Fig. 3b). On removing the nitrogen by pumping this positive rate rises slightly (Fig. 3c.). When the water filter is removed the rate rises, at first sharply showing a small maximum, falls slightly and then rises again steadily (Fig. 3d). On restoring the water filter the rate gradually falls to its initial constant value (Fig. 3e). Fig. 3f shows that the negative rate is related to the extent of decomposition. In this case, a much higher negative rate is observed after the sample has been decomposed considerably. That this negative rate is also related to the pressure of nitrogen in the system is shown by opening the system to the pumps, when the rate rapidly increases to its constant positive value (Fig. 3g).

*Cæsium Azide.*—Fig. 4 shows plots of the rate of photolysis against the number of nitrogen molecules evolved for 200 mg. samples of cæsium azide at  $0^\circ$  (Curve a) and  $-80^\circ$

(Curve b). The intensities of irradiation were  $1.22 \times 10^{15}$  and  $1.79 \times 10^{15}$  quanta  $\text{cm}^{-2} \text{sec}^{-1}$ , respectively. Both curves show a decreasing rate, tending to become constant with a point of inflexion (a run at room temperature showed similar features). The activation energy was calculated by measuring the rates at three temperatures, after these had become reasonably constant. The approximate value of the activation energy found is  $1.7 \text{ kcal. mole}^{-1}$  for the final, constant rate.\* The intensity-dependence of the constant rate was determined at  $-80^\circ$ , the dark rate being negligible at this temperature. The rate varies linearly with intensity (Fig. 5). When the sample is left in

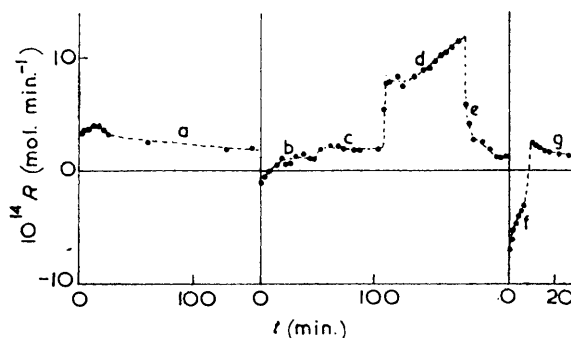


FIG. 3. Photolysis of rubidium azide through a water filter. (a) Fresh sample. (b) After being in contact with nitrogen for 16 hr. (c) Nitrogen pressure removed. (d) After removal of the water filter. (e) Water filter replaced. (f) After being in contact with nitrogen for 18 hr. (g) Nitrogen pressure removed.

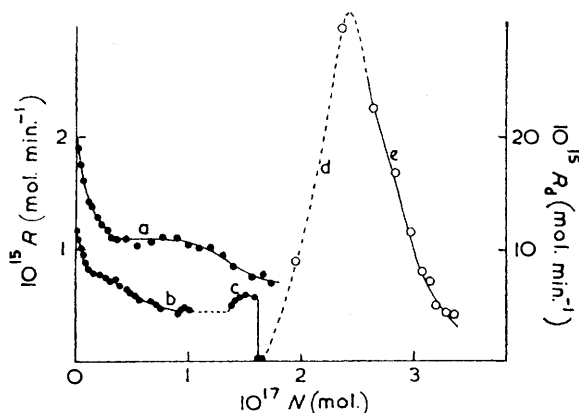


FIG. 4. Photolysis of caesium azide. (a) At  $0^\circ$  and an intensity  $1.22 \times 10^{15}$  quanta  $\text{cm}^{-2} \text{sec}^{-1}$ . (b) At  $-80^\circ$  and an intensity of  $1.77 \times 10^{15}$  quanta  $\text{cm}^{-2} \text{sec}^{-1}$ . (c) After leaving the sample in contact with nitrogen for 18 hr. at  $-80^\circ$ . (d) and (e) Dark rate as the sample is warmed up to  $24^\circ$ .  $N$  is the total number of nitrogen molecules produced in the reaction.

contact with nitrogen at  $-80^\circ$  for 18 hr., the subsequent rate of photolysis does not decrease (Fig. 4, Curve c). After a total irradiation of 258 min. at an intensity of  $1.79 \times 10^{15}$  quanta  $\text{cm}^{-2} \text{sec}^{-1}$ , the lamp was switched off and the sample then allowed to warm up to room temperature ( $24^\circ$ ). The dark rate rises to a very high value (Fig. 4, Curve d) and then decreases gradually (Fig. 4, Curve e). The ratio  $g_d/g_l$  is 1.6.

The same sample was then left open to the pumps for two weeks at room temperature.

\* The order of magnitude of  $E$  is not affected by our lack of knowledge of the precise temperature when the reaction vessel is immersed in a bath at  $-80^\circ$ .

The decomposition of the sample after this period of conditioning was closely similar (Fig. 6, Curve a) to that obtained previously (Fig. 4, Curve c), the constant rates being the same. The lamp was then switched off and the sample allowed to warm up first to 0° and then to 22°. The variation of dark rate with the number of nitrogen molecules evolved is shown in Fig. 6, Curves b and c. The activation energy associated with the dark process is approximately 19 kcal. mole<sup>-1</sup>. The ratio  $g_d/g_t$  is again 1.6. If the sample is now left in contact with nitrogen for 19 hr. at room temperature and then photolysed at this temperature, the rate of photolysis is initially zero, and then rises gradually to its final constant value (Fig. 6, Curve d). The subsequent dark reaction is shown in Fig. 6, Curve e. The ratio  $g_d/g_t$  is 0.65 at room temperature. The plots of  $R_d^{1/2}$  against  $N_d$  for all these dark reactions are shown in Fig. 7A and B.

FIG. 5. Intensity-dependence of the constant rate at  $-80^\circ$  for cæsium azide.

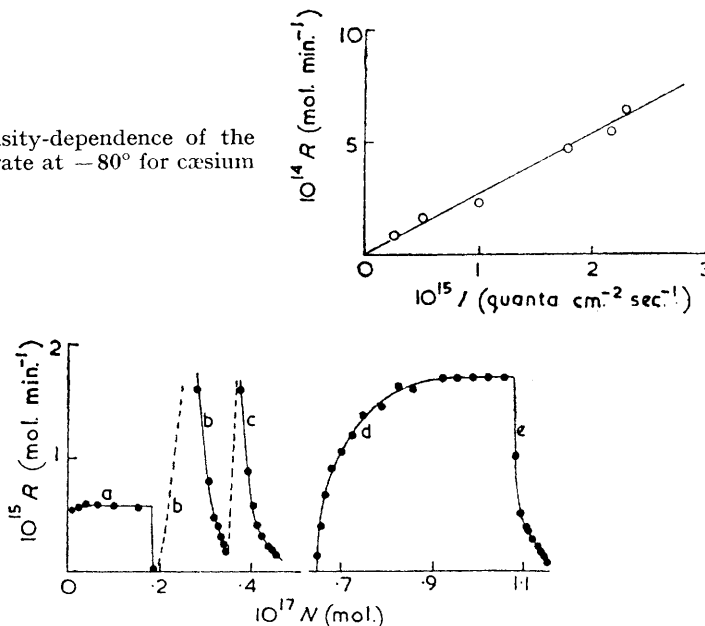


FIG. 6. Rate of decomposition of the same sample as in Fig. 4 after it had been conditioned at room temperature *in vacuo*. (a) Photolysis at  $-80^\circ$ . (b) Dark rate as the sample is warmed up to  $0^\circ$ . (c) Dark rate as the sample is warmed up from  $0^\circ$  to  $24^\circ$ . (d) Photolysis after the sample has been left in contact with nitrogen for 19 hr. at room temperature. (e) Subsequent dark rate.  $N$  is the total number of molecules of nitrogen produced in the reaction.

When a fresh sample of cæsium azide is irradiated under similar conditions at room temperature ( $24^\circ$ ), except that the irradiation from the L.P. lamp is filtered through a water filter, the plot of the rate of photolysis against the number of nitrogen molecules evolved shows the same decelerative character, but the point of inflexion does not occur (Fig. 8, Curve a). The rates are much smaller and the dark reaction negligible (Fig. 8, Curve b). The rate after the sample has been left in contact with nitrogen for 17 hr. is shown in Fig. 8, Curve c; Fig. 8, Curve d shows the behaviour when the water filter is removed and Fig. 8, Curve e the effect of removing nitrogen by pumping.

The mechanism of the photochemical decomposition of potassium azide<sup>10</sup> and sodium azide<sup>11</sup> has been discussed previously. Potassium, barium<sup>9</sup> and strontium<sup>10</sup> azides all show decelerative and accelerative phases as does rubidium azide (Fig. 1). Consequently, two mechanisms for the photolytic decomposition were postulated<sup>9,10</sup> but, when the decomposition of sodium azide was studied in detail, it was found that the constant-rate

process is not a continuation of the initial decelerative process but a new process altogether. Irradiated through a water filter, potassium and barium azides behave like the sodium salt. Thus three mechanisms for the photolytic decomposition are required to explain the experimental results. Only two occur in sodium azide.<sup>11</sup> In salt that has not been previously irradiated, photochemically excited azide ions<sup>14</sup> are trapped at special sites in the crystal and decompose bimolecularly to yield nitrogen and metal (nucleus formation). The metal produced by the first reaction catalyses the second process. The metal nuclei

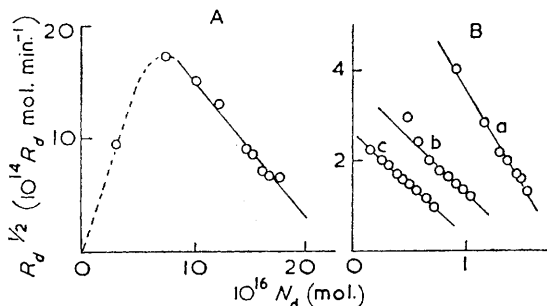


FIG. 7. Square-root dependence of the dark rate  $R_d$  on  $N_d$ , the number of molecules of nitrogen produced in the dark reaction, illustrating second order kinetics.

A. Data from Fig. 4d and e.

B. Second-order plots for the dark reaction at (a) 0°; (b) and (c) 24°.

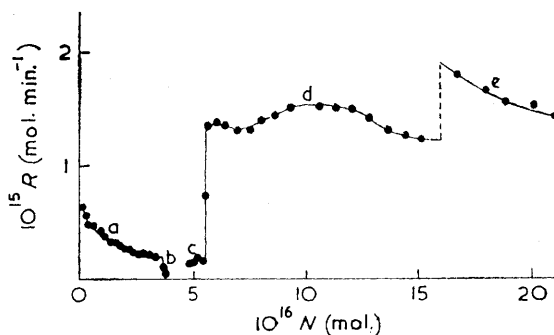


FIG. 8. Photolysis of caesium azide at 24° through a water filter. (a) Fresh sample; (b) dark reaction; (c) photolysis after leaving the sample in contact with nitrogen for 17 hr; (d) rate when the water filter is removed; (e) rate on removing the nitrogen pressure by pumping.  $N$  is the total number of nitrogen molecules produced in the reaction.

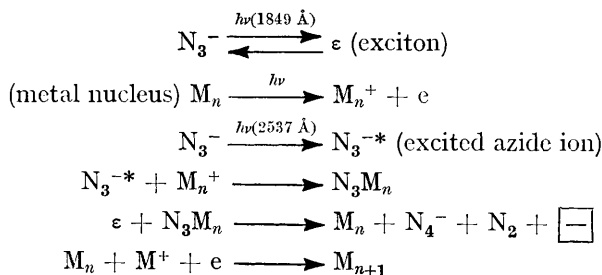
become ionised by photoemission and thus act as intermediates for the transfer of electrons from excited ions to sodium ions, the sodium atoms formed being added to the nuclei, which thus grow. The constant rate of reaction is consistent with a constant, linear growth-rate, and it has been shown<sup>11</sup> that the kinetics of the photolysis of sodium azide are consistent with the hypothesis of random nucleation and a linear growth of nuclei.

The accelerative process found in all the other azides investigated, apart from caesium azide (Fig. 4) to which special considerations apply (see later), cannot be explained by assuming a measure of two- or three-dimensional growth of nuclei, because the accelerative process requires photons of higher energy. Light of wavelength 1849 Å lies within the true exciton band for potassium azide, and so it may be that the third process involves excitons rather than excited azide ions. The band structures of sodium and potassium azides, are very similar, however, and so it is difficult to see why the accelerative process does not occur in sodium azide, unless it is because of their different crystal structures.

<sup>14</sup> Deb, *J. Chem. Phys.*, 1961, **35**, 2122.

The accelerative process and the dark reaction seem to be related, for the dark reaction is not pronounced in sodium azide. We therefore believe that the dark reaction is due to the thermal decomposition of an unstable intermediate formed during the accelerative reaction; this unstable species could be the  $N_4^-$  molecular ion.<sup>15,10</sup> The thermal decomposition of unexcited azide ions, a mechanism proposed earlier for barium azide,<sup>9</sup> is unlikely to hold for potassium azide, which is much more stable. Positive holes ( $N_3$ ) and excited azide ions would not be sufficiently stable, but  $N_4^-$  ions have about the right stability. Furthermore  $N_4^-$  has not been identified in sodium azide.

We thus arrive at the following mechanism for the acceleratory reaction.



In these equations  $M_n$  denotes a metal nucleus containing  $n$  atoms and  $\square$  an anion vacancy.

If none of the  $N_4^-$  ions formed decomposed during irradiation, the amount of gas

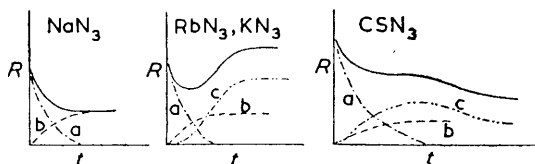


FIG. 9. Schematic plots of rate against time for the photolysis of alkali metal azides showing how the overall rate curve can be obtained from two or three separate curves. (a) Reaction at defect sites. (b) Linear growth of metal nuclei. (c) Rate due to the decomposition of  $N_4^-$ .

evolved in the dark reaction should be *twice* that evolved by this process in the photochemical reaction. Experimentally, the ratio  $g_d/g_l$  is about 1.6 at  $-80^\circ$ . The ratio measured will always in fact be less than 2, because there are two mechanisms for the light reaction, the linear growth process and the accelerative process; only the second of these produces  $N_4^-$ . At room temperature, the ratio  $g_d/g_l$  is much smaller (0.24 and 0.65), because there is considerable thermal decomposition of  $N_4^-$  ions going on concurrently with the photolysis reaction.

The special shape of the rate curves for caesium azide is not due to the more pronounced rate of attack of the metal by nitrogen gas, although there is a more than 50% increase in rate on pumping out the evolved gas (Fig. 8). Similar, but much smaller, effects occur with potassium and rubidium azide. However, a dynamic run, in which the nitrogen is pumped out between each reading, shows the same shape as Fig. 4a. Nevertheless, the reaction that produces an accelerative process in potassium, rubidium and caesium azides does occur, as shown by the increase in rate measured when the water filter is removed. The contributions of the three mechanisms of photolytic decomposition to the total rate curve are shown in Fig. 9 for the three observed cases, typified by sodium azide, rubidium azide and caesium azide. (a) is the initial decelerative reaction, (b) the linear growth and (c) the accelerative process involving the production of  $N_4^-$ .

<sup>15</sup> Shuskus, Young, Gilliam, and Levy, *J. Chem. Phys.*, 1961, **35**, 1442.

The dark reaction is of second order kinetically, as shown by the linear plots in Figs. 2 and 7. This is difficult to understand if it is indeed the decomposition of  $N_4^-$  ions. Possibly, all that we have said for  $N_4^-$  applies to some other, as yet undiscovered, intermediate in the decomposition of azides.

A further feature of interest is the *photochemical* reaction that has been found to occur between nitrogen and rubidium metal (Figs. 3b and f). The data available do not, however, permit any detailed discussion of the phenomenon at this stage.

[*Note Added in Proof.*—A probable mechanism is  $N_4^- \longrightarrow N_3^- + N$ , followed by  $N + N \longrightarrow N_2$ . This satisfies the bimolecular kinetics without requiring mobility of  $N_4^-$  ions.]

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IMPERIAL COLLEGE, LONDON S.W.7.

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