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## THE IONIZATION OF NITROUS OXIDE AND NITROGEN DIOXIDE BY ELECTRON IMPACT

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## ABSTRACT

The same apparatus used for the study of  $\text{CO}_2$  has now been used to study the products of ionization in  $\text{NO}_2$  and  $\text{N}_2\text{O}$ . Thermal dissociation is so serious in  $\text{NO}_2$  that the results are somewhat unsatisfactory but  $\text{NO}_2^+$ ,  $\text{N}^+$  and  $\text{O}_2^+$  are found as primary ions and their appearance potentials determined approximately. In  $\text{N}_2\text{O}$  the results were more satisfactory and the appearance potentials 12.9, 16.3, 15.3, 21.4 were found for the primary ions  $\text{N}_2\text{O}^+$ ,  $\text{O}^+$ ,  $\text{NO}^+$ ,  $\text{N}^+$  respectively. In both gases other primary ions were probably present but obscured by ions from products of thermal dissociation. As in  $\text{CO}_2$  the observed potentials agreed within the limits of error with calculated values.

PURSUING the general scheme of investigating the simplest triatomic molecules the authors went on from the experiment on carbon dioxide reported in the preceding paper to study the products of ionization in nitrous oxide and nitrogen dioxide. These substances have almost the same advantages as  $\text{CO}_2$  as far as our knowledge of their structure is concerned. Not only are the heats of dissociation of the gases themselves known but also the heats of dissociation and ionization potentials of their constituent parts,  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{NO}$ ,  $\text{N}$  and  $\text{O}$ . Furthermore both  $\text{N}_2\text{O}$  and  $\text{NO}_2$  are supposed to be triangular in structure furnishing an interesting contrast with  $\text{CO}_2$  which is linear.

Experimentally, however, difficulties of two sorts arose. The first, which was foreseen, was the high degree of thermal dissociation which made any study of pressure variations futile and all results more difficult of interpretation. The second difficulty was a variable error in the voltage scale which made corrections uncertain and the determination of some of the ionization potentials less accurate than in  $\text{CO}_2$ .

## EXPERIMENTS AND RESULTS

The apparatus and procedure were the same as those described in the preceding case except that the electrode in front of the filament was changed from nickel to platinum and two fine wires welded across the hole  $O$  to make the field more uniform. (see Fig. 1 in previous paper).

The  $\text{NO}_2$  was generated by heating  $\text{Pb}(\text{NO}_3)_2$  and purified by fractional distillation. In the ionization chamber it was dissociated to such an extent that a typical mass spectrum showed  $\text{NO}^+$  ions ten times more numerous than  $\text{NO}_2^+$  and showed some  $\text{N}_2^+$  and  $\text{O}_2^+$  ions present. Therefore the possibility must be considered that the  $\text{NO}^+$ ,  $\text{O}^+$  and  $\text{N}^+$  ions observed came from ionization of  $\text{NO}$ ,  $\text{N}_2$  or  $\text{O}_2$  rather than directly from  $\text{NO}_2$ .

The  $\text{N}_2\text{O}$  was generated by heating  $\text{NH}_4\text{NO}_3$  and was dried over  $\text{P}_2\text{O}_5$ . The dissociation difficulty appeared here also but with certain differences. In this case the  $\text{N}_2\text{O}^+$  was the strongest ion with  $\text{O}_2^+$  and  $\text{N}_2^+$  much stronger

and NO<sup>+</sup> relatively weaker than in the NO<sub>2</sub> mass spectrograms. But again care must be taken in interpreting results though in general they are better than in NO<sub>2</sub>.

Fortunately the resolution of the apparatus was excellent. Therefore it was possible to observe the appearance potentials of nearly all the stronger ions. The only exceptions were N<sub>2</sub><sup>+</sup> and O<sub>2</sub><sup>+</sup> in NO<sub>2</sub> where the great intensity of NO<sup>+</sup> obscured the appearance potentials of the neighboring ions.

Early in the experiments on NO<sub>2</sub> it was noticed that the appearance potential of NO<sup>+</sup> was not as far below that of argon as might be expected. Therefore it was decided to use the ionization potential of mercury as a second calibration point for correction of observed voltages. As may be seen in the tables below, this gave the surprising result that the observed appearance potential of the Hg<sup>+</sup> ion was only about 3.8 volts below that of the A<sup>+</sup> ion instead of the 5.2 which it should be. This is attributed to some variable charged layer or possibly some geometrical effect. Attempts were made to diagnose it more exactly by measuring the velocity and intensity characteristics of electrons reaching probes inserted just behind the hole *O*, or just above the slit *S*<sub>1</sub> (see Fig. 1 in previous paper) but the results were inconclusive. However plotting the observed values for A<sup>+</sup>, CO<sub>2</sub><sup>+</sup> and Hg<sup>+</sup> against their true values a correction curve can be drawn and observations of unknown ionization potentials corrected by it. Actually such an interpolation is required in only one case, N<sub>2</sub>O<sup>+</sup>. Of the other three ions appearing below 14 volts, NO<sup>+</sup> and NO<sub>2</sub><sup>+</sup> both appear at approximately the same place as Hg<sup>+</sup> while the O<sub>2</sub><sup>+</sup> in the N<sub>2</sub>O appears by interpolation at 13.5 which is in agreement with the accepted value of the oxygen ionization potential.

A typical ionization potential curve for N<sub>2</sub>O is shown in Fig. 1 and the results of a number of runs on NO<sub>2</sub> and N<sub>2</sub>O are tabulated below.

TABLE I.  
A. NO<sub>2</sub>

Run	<i>P</i>	Observed Ionization Potential					
		Hg <sup>+</sup>	NO <sub>2</sub> <sup>+</sup>	NO <sup>+</sup>	A <sup>+</sup>	O <sup>+</sup>	N <sup>+</sup>
2	7 × 10 <sup>-4</sup>		15.0	14.5	18.2		
3	11		17.5	17.2	20.9		
4	10		17.0	16.5	18.9		
5	9 NO gas			17.5	20.0		
6	10		15.0	15.0	18.5	20.5	
7	10	14.5		14.5			
8	12		15.75	15.5	18.5	20.7	23.7

B. N<sub>2</sub>O

Run	<i>P</i>	Observed Ionization Potentials (with weights)							
		Hg <sup>+</sup>	N <sub>2</sub> O <sup>+</sup>	NO <sup>+</sup>	A <sup>+</sup>	O <sub>2</sub> <sup>+</sup>	N <sub>2</sub> <sup>+</sup>	O <sup>+</sup>	N <sup>+</sup>
1	25 × 10 <sup>-4</sup>		16.5(10)		19.0(10)				
2	18	13.8(10)	15.2(10)		17.3(10)				
3	7	13.6(10)	15.0(10)						
4	12	13.5(10)	15.0(10)		17.5(10)				
5	7		16.1(10)	18.3(10)			18.5(10)	19.7(2)	25.5(2)
6*	12		16.5(10)	18.3(10)		17.0(10)	18.7(10)	19.5(2)	24.5(2)
7	12		16.5(10)	17.8(2)	18.5(2)	17.0(10)	18.5(2)		

\* Run shown in Fig. 1.

By using argon and mercury as reference points and using the correction curve discussed above we arrive at the following experimental values where

TABLE II

From	NO <sub>2</sub> <sup>+</sup>	N <sub>2</sub> O <sup>+</sup>	NO <sup>+</sup>	O <sub>2</sub> <sup>+</sup>	N <sub>2</sub> <sup>+</sup>	O <sup>+</sup>	N <sup>+</sup>
NO <sub>2</sub>	11.0?		10.5?			17.7?	20.8?
N <sub>2</sub> O		12.9	15.3	13.5	15.5	16.3?	21.4

the question marks indicate that the accuracy is poor, perhaps 10% and we refrain deliberately from giving estimated errors for each separate potential. The ones not questioned are probably accurate to about half a volt.

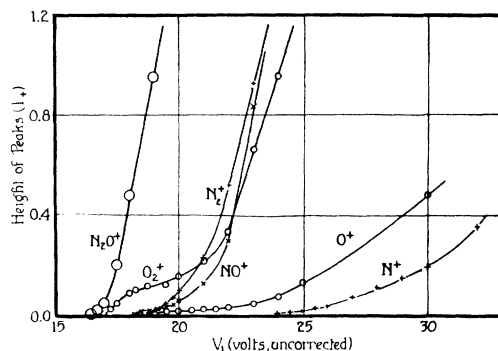


Fig. 1.

## DISCUSSION

In comparing these experimental results with theoretical values we must remember that we can safely attribute an ionizing potential to NO<sub>2</sub> or N<sub>2</sub>O

TABLE III.

Process	Heats of dissociation	Volts	Ionizing potentials
	NO <sub>2</sub> → N + O <sub>2</sub>	4.3	N <sub>2</sub> 16.5 <sup>2</sup>
	NO <sub>2</sub> → NO + O	3.3	N 14.5 <sup>3</sup>
	N <sub>2</sub> O → N <sub>2</sub> + O	2.0	O <sub>2</sub> 13.5 <sup>4</sup>
	N <sub>2</sub> O → NO + N	4.6	O 13.5 <sup>5,3</sup>
	NO → N + O	6.5	NO 9.4 <sup>6</sup>
	N <sub>2</sub> → N + N	9.1	A 15.6 <sup>3</sup>
	O <sub>2</sub> → O + O	5.6	Hg 10.4 <sup>3</sup>

only of the observed value is lower than the theoretical value for production from N<sub>2</sub>, O<sub>2</sub>, or NO. Even the assurance of the chemists that no NO is to

<sup>1</sup> Mecke, Z. its. f. Phys. Chem. **B7**, 108-129 (1930).

<sup>2</sup> Estimated most probable value. Authorities differ.

<sup>3</sup> Russell, Astrophys. J. **70**, 16 (1929).

<sup>4</sup> Stueckelberg, Phys. Rev. **34**, 65 (1929).

<sup>5</sup> Frerichs, Phys. Rev. **34**, 1239 (1929).

<sup>6</sup> Birge, International Critical Tables, Vol. 5.

be expected in  $N_2O$  must be regarded with skepticism at first though it will be seen later to be verified. With the heats of dissociation given by Mecke<sup>1</sup> and the ionizing potentials from various sources given in Table II the minimum energy can be calculated for fifteen of the seventeen possible processes, which might be expected to occur in  $NO_2$  or  $N_2O$ . The two ionization potentials that can not be predicted are, of course, simple ionization of  $N_2O$  and  $NO_2$  without any dissociation. Without considering in detail the processes which might lead to each type of ion we may take one as typical. Consider  $NO^+$ . In  $NO_2$  it could be produced directly from  $NO_2$  at 12.7 volts but actually it appears very strongly below this point so that presumably it comes from  $NO$  present as the result of dissociation and requiring only 9.5 volts for ionization. On the other hand in  $N_2O$ ,  $NO^+$  first appears at about 15.3 volts whereas it can first be produced directly from  $N_2O$  at 14.0. This suggests that it is actually being produced in this way and that there is no appreciable amount of  $NO$  itself present. This confirms the views of the chemists on the nature of dissociation in  $N_2O$  and allows us to throw out  $NO$  as a possible source of  $N^+$  or  $O^+$  in the experiments on  $N_2O$ . The results of arguments of this type are embodied in Table IV below.

TABLE IV.

Process	Theor.	Obs.	Remarks
$NO_2 \rightarrow NO_2^+$		11.0	
$\rightarrow NO^+ + O$	12.7		Obscured by $NO \rightarrow NO^+$
$\rightarrow NO + O^+$	16.8	17.7	Definitely occurs
$\rightarrow N + O_2^+$	17.8		$O_2^+$ present but I.P. obscured by $NO^+$
$\rightarrow N^+ + O_2$	18.8	20.8	Uncertain, perhaps due to $NO$
$N_2O \rightarrow N_2O^+$		12.9	
$\rightarrow N_2 + O^+$	15.5	16.3	Definitely occurs
$\rightarrow N_2^+ + O$	18.5		Obscured by $N_2 \rightarrow N_2^+$
$\rightarrow NO^+ + N$	14.0	15.3	Reasonably certain
$\rightarrow NO + N^+$	19.1	21.4	Reasonably certain

It seems that in every case where a definite conclusion can be drawn it is to the effect that the process to be expected does occur and at nearly the minimum possible energy. Perhaps the most interesting processes are  $NO_2 \rightarrow N^+ + O_2$  and  $N_2O \rightarrow N_2 + O^+$  which evidently do occur although the corresponding process  $CO_2 \rightarrow C^+ + O_2$  does not occur. This is in perfect accord with our ideas as to the difference in structure of these molecules.

These results combined with those on  $CO_2$  give a most satisfactory confirmation of predictions of ionization phenomena by the use of thermochemical data, a process that fell into disrepute after its early failure in the case of  $HCl$ . Unfortunately there are few other triatomic molecules for which we have sufficient data to make predictions. However the authors hope to continue the work as well as possible.