THE IONIZATION OF NITROUS OXIDE AND NITROGEN DIOXIDE BY ELECTRON IMPACT

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Abstract

The same apparatus used for the study of CO_2 has now been used to study the products of ionization in NO_2 and N_2O. Thermal dissociation is so serious in NO_2 that the results are somewhat unsatisfactory but NO_2^+, N^+ and O_2^+ are found as primary ions and their appearance potentials determined approximately. In N_2O the results were more satisfactory and the appearance potentials 12.9, 16.3, 15.3, 21.4 were found for the primary ions N_2O^+, O^+, NO^+, N^+ respectively. In both gases other primary ions were probably present but obscured by ions from products of thermal dissociation. As in CO_4 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 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, N_2, O_2, NO, N and O. Furthermore both N_2O and NO_2 are supposed to be triangular in structure furnishing an interesting contrast with 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 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 NO_2 was generated by heating $Pb(NO_3)_2$ and purified by fractional distillation. In the ionization chamber it was dissociated to such an extent that a typical mass spectrum showed NO^+ ions ten times more numerous than NO_2^+ and showed some N_2^+ and O_2^+ ions present. Therefore the possibility must be considered that the NO^+, O^+ and N^+ ions observed came from ionization of NO, N_2 or O_2 rather than directly from NO_2.

The N_2O was generated by heating NH_4NO_3 and was dried over P_2O_5. The dissociation difficulty appeared here also but with certain differences. In this case the N_2O^+ was the strongest ion with O_2^+ and N_2^+ much stronger

and NO^+ relatively weaker than in the NO_2 mass spectrograms. But again care must be taken in interpreting results though in general they are better than in NO_2.

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_2^+ and O_2^+ in NO_2 where the great intensity of NO^+ obscured the appearance potentials of the neighboring ions.

Early in the experiments on NO_2 it was noticed that the appearance potential of NO^+ 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^+ ion was only about 3.8 volts below that of the A^+ 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_1 (see Fig. 1 in previous paper) but the results were inconclusive. However plotting the observed values for A^+, CO_2^+ and Hg^+ 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_2O^+. Of the other three ions appearing below 14 volts, NO^+ and NO_2^+ both appear at approximately the same place as Hg^+ while the O_2^+ in the N_2O 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_2O is shown in Fig. 1 and the results of a number of runs on NO_2 and N_2O are tabulated below.

TABLE I.
A. NO_2

Run	P	Hg⁺	Observed Ionization Potential				
			NO₂⁺	NO⁺	A⁺	O⁺	N⁺
2	7×10^{-4}		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_2O

Run	P	Hg⁺	Observed Ionization Potentials (with weights)						
			N₂O⁺	NO⁺	A⁺	O₂⁺	N₂⁺	O⁺	N⁺
1	25×10^{-4}		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_2^+	N_2O^+	NO^+	O_2^+	N_2^+	O^+	N^+
NO_2	11.0?		10.5?			17.7?	20.8?
N_2O		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.
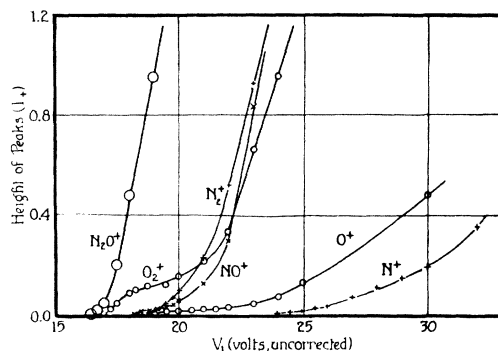

Fig. 1.

DISCUSSION

In comparing these experimental results with theoretical values we must remember that we can safely attribute an ionizing potential to NO_2 or N_2O

TABLE III.

Process	Heats of dissociation Volts	Ionizing potentials	
$NO_2 \rightarrow N+O_2$	4.3	N_2	16.5[2]
$NO_2 \rightarrow NO+O$	3.3	N	14.5[3]
$N_2O \rightarrow N_2+O$	2.0	O_2	13.5[4]
$N_2O \rightarrow NO+N$	4.6	O	13.5[5,3]
$NO \rightarrow N+O$	6.5	NO	9.4[6]
$N_2 \rightarrow N+N$	9.1	A	15.6[3]
$O_2 \rightarrow O+O$	5.6	Hg	10.4[3]

only of the observed value is lower than the theoretical value for production from N_2, O_2, or NO. Even the assurance of the chemists that no NO is to

[1] Mecke, Z its. f. Phys. Chem. B7, 108–129 (1930).
[2] Estimated most probable value. Authorities differ.
[3] Russell, Astrophys J. 70. 16 (1929).
[4] Stueckelberg, Phys. Rev. 34, 65 (1929).
[5] Frerichs, Phys. Rev. 34, 1239 (1929).
[6] 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[1]
and the ionizing potentials from various sources given in Table II the mini-
mum 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 poten-
tials 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 con-
firmation of predictions of ionization phenomena by the use of thermo-
chemical 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.