to develop a new and practical method for the preparation of nitrogen ring compounds of the phenanthridine type. 9-Methyl-, 9-phenyl- and 9-(α-naphthyl)-9-fluorylchloroamine have been converted to 9-methyl-, 9-phenyl- and 9-(α-naphthyl)-phenanthridine. That this method is not restricted to the halogenoamines is indicated by the thermal conversion of 9-(α-naphthyl)-9-fluorylazide to 9-(α-naphthyl)-phenanthridine. The primary factor in directing the course of the rearrangement of the intermediate free radical seems to be the highly strained condition of the five-membered ring in biphenylenemethylene, rather than the electronegativities of the radicals attached to the tertiary carbon atom.

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[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 572]

The Adjacent Charge Rule and the Structure of Methyl Azide, Methyl Nitrate, and Fluorine Nitrate

BY LINUS PAULING AND L. O. BROCKWAY

With the recognition of the fact that in many cases the normal state of a molecule cannot be represented satisfactorily by a single valence-bond structure of the Lewis type but can be approximated by a combination of several such structures (among which it is said to resonate) there arose the problem of determining for each resonating molecule the magnitudes of the contributions of various reasonable structures. Information regarding these magnitudes is being obtained in many ways, such as from the interpretation of experimental values of interatomic distances, force constants, electric dipole moments, etc., and some progress is being made in the formulation of empirical rules expressing this information in a succinct form. Four years ago it was pointed out[1] that the observed moment of inertia of nitrous oxide corresponds to resonance between the structures $:\overset{-}{\ddot{N}}=\overset{+}{N}=\ddot{O}:$ and $:N\equiv\overset{+}{N}-\underset{..}{\overset{-}{\ddot{O}}}:$, the third reasonable structure, $:\underset{..}{\overset{=}{\ddot{N}}}-\overset{+}{N}\equiv\overset{+}{O}:$, making no appreciable contribution, whereas the closely similar molecule carbon dioxide resonates among all three analogous structures; and in explanation of this unexpected fact the suggestion was advanced that, in general, structures in which adjacent atoms have electrical charges of the same sign are much less important than other structures, the diminution in importance resulting from the increase in coulomb energy corresponding to the adjacent charges. This *adjacent charge rule* was reported also to apply to the methyl azide molecule.[2] We have now reinvestigated methyl azide by electron diffraction and have similarly studied methyl nitrate and fluorine nitrate. The configurations found for all of these substances are those predicted on the basis of the rule.

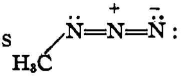
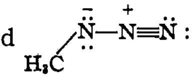
Methyl Azide.—In our earlier investigation of methyl azide[2] it was concluded that the molecules contain a linear azide group with dimensions corresponding to resonance between the structures  and . The photographs used in this work were very light, showing only one measurable apparent maximum and one minimum. With improved technique we have now obtained photographs of methyl azide showing five well-defined apparent maxima, the interpretation of which has led to the verification and refinement of the earlier results. The

TABLE I

METHYL AZIDE

Max.	Min.	I	s, obsd	s, calcd. for model H-120°	s, calcd. for model I-120°	C–N for model H-120°, Å.	C–N for model I-120°, Å.
1		5	6.17	6.15	6.28	1.465	1.496
2		2	8.32	8.26	8.36	1.460	1.477
	3		10.20	9.70	10.15	1.397	1.461
3		3	11.49	11.49	11.77	1.470	1.507
	4		12.75	12.47	12.70	1.437	1.464
4		1	13.81	13.68	13.66	1.455	1.454
	5		15.54	15.20	15.38	1.438	1.455
5		1	16.77	17.12	17.40	1.500	1.524
				Average C–N	=	1.453	1.480
				N–N′	=	1.246	1.229
				N′–N″	=	1.087	1.107

Averaged results: C–N = 1.47 ± 0.02 Å.
N–N′ = 1.24 ± 0.02 Å.
N′–N″ = 1.10 ± 0.02 Å.
Angle C–N–N = 120 ± 5°

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[1] L. Pauling, *Proc. Nat. Acad. Sci.*, **18**, 498 (1932).

[2] L. O. Brockway and L. Pauling, *ibid.*, **19**, 860 (1933).

sample of methyl azide used was part of that prepared for the first investigation by Dr. G. W. Wheland. The photographs were taken with a film distance of about 10 cm. and electron wave lengths of about 0.06 Å.

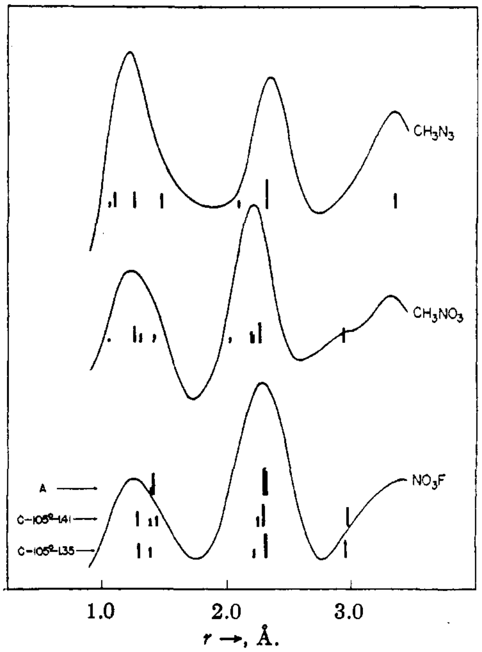
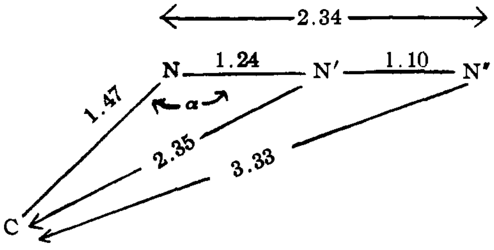


Fig. 1.—Radial distribution curves for methyl azide, methyl nitrate, and fluorine nitrate.

The measured s values and estimated intensities, averaged for sixteen photographs, given in Table I lead to the radial distribution curve shown in Fig. 1, with principal peaks at 1.22, 2.34, and 3.33 Å. These correspond closely with C–N = 1.47 Å. (the sum of the single-bond covalent radii), N–N = 1.24 and 1.10 Å., and the C–N–N angle = 120°, the peak at 1.22 Å. representing the unresolved distances 1.10, 1.24, and 1.47 Å. This correspondence was verified in the usual way by the comparison of the photographs with calculated intensity curves. In Fig. 2 there are shown curves for models containing a linear azide group,[3] defined by the following values of the distances N–N′ and N′–N″, respectively: E, 1.10, 1.10; F, 1.26, 1.26; G, 1.26, 1.16; H, 1.26, 1.10; I, 1.22, 1.10; the angle α having the value 180° for E and 125° for F and G, and the values shown for H and I. The C–N distance was assumed to be 1.47 Å., the C–H distances 1.06 Å., and the carbon angles were assumed to be tetrahedral. All interactions were considered, with one orientation of the methyl group.



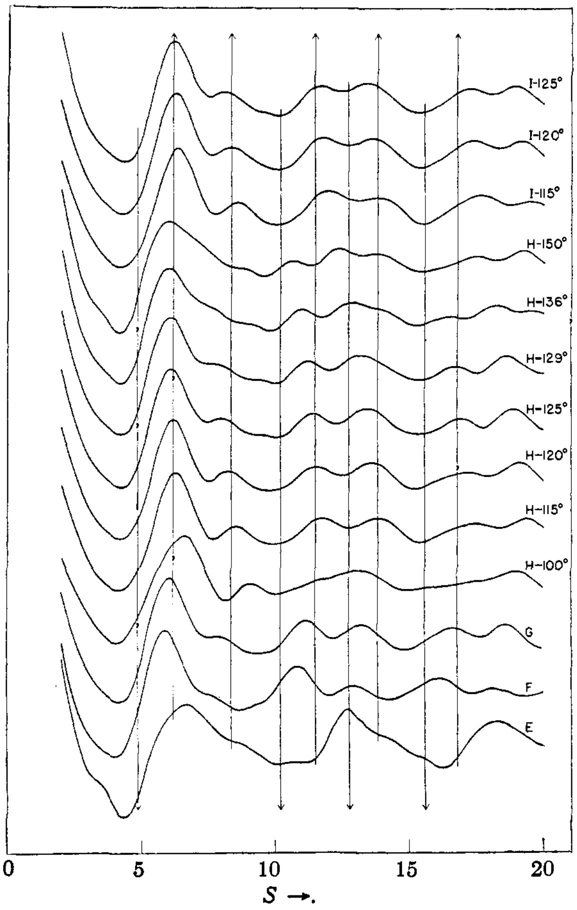


Fig. 2.—Theoretical intensity curves for methyl azide.

It is seen that all of the curves show pronounced disagreement with the photographs except H-120° and I-120° and their immediate neighbors. For these curves the qualitative and quantitative comparisons are satisfactory. The agreement for the second, third, and fourth peaks is somewhat better for the 120° curves than for the 115 or 125° curves, and we accept for the nitrogen bond angle the value 120 ± 5°, which is at the lower edge of the range of values 135 ± 15°

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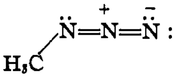
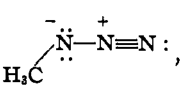
[3] The new photographs, like the old ones, are incompatible with a cyclic configuration.

previously reported. The quantitative comparison (Table I) leads to the interatomic distances C–N = 1.47 ± 0.02 Å., N–N′ = 1.24 ± 0.02 Å., and N′–N″ = 1.10 ± 0.02 Å. This final configuration of the model is identical with that indicated by the radial distribution curve.

These results are in good accord with the assumption that the molecule resonates between the two electronic structures  and , the N–N′ distance having essentially the double-bond value and the N′–N″ distance the triple-bond value.[4] The value 120° for the nitrogen bond angle, intermediate between those expected for a single and a double bond (125° 16′) and for two single bonds (109° 28′)., is also not unreasonable.

Methyl Nitrate.—Methyl nitrate was prepared from methyl alcohol, nitric acid, and urea nitrate by Mr. Willard McRary under the direction of Professor H. J. Lucas. The product was washed repeatedly with water and dried, and then was redistilled three times.

The photographs show six well-defined and nearly uniformly separated rings, with *s* values and estimated intensities as given in Table II.

TABLE II

METHYL NITRATE

Max.	Min.	I	*s*, obsd.	*s*, calcd. for model II-105°	*s*, calcd./*s*, obsd.
1		1	3.50	3.23	(0.923)
	2		4.67	4.17	(0.893)
2		5	6.34	6.34	1.000
	3		7.92	7.98	1.008
3		3	9.44	9.40	0.996
	4		10.69	10.50	.982
4		2	11.93	11.60	.973
	5		13.50	13.18	.976
5		1	14.87	15.20	1.022
	6		16.21	16.50	1.018
6		1	17.71	17.68	.998
				Average	0.997

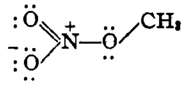
Results (model II–105°): N–O = 1.26, 1.26, 1.36 Å.

O–C = 1.43 Å.

Angle N–O–C = 105 ± 5°

The six-term radial distribution function (Fig. 1) has a broad peak at about 1.24 Å., a sharper peak at 2.21 Å., and another at 3.32 Å. These are compatible with the models discussed below, but provide no basis for choice among them.

The number of parameters determining the structure of the molecule is so great that it was not possible to carry out a thorough investigation involving their independent variation. We have accordingly contented ourselves with the attempt to decide between the two most reasonable structures. The first, representing resonance among the three structures A, B, and C, leads to the predicted dimensions shown below, all three N–O bonds having approximately the double bond distance. The methyl group is restricted to the plane of the nitrate group by the double-bond character of the N–OCH$_3$ bond. For α a value of about 120 or 125° would be expected; curves calculated for 120, 125, and 130° are shown in Fig. 3. The second reasonable structure, representing resonance between A and B only, corresponds to essentially the double-bond distance for two of the N–O bonds and the single-bond distance for the third. Steric effects probably tend to keep the methyl group out of the plane of the nitrate group. The curves of Fig. 3 are calculated on this assumption; we have found that they are changed only slightly by the assumption of free rotation of the OCH$_3$ group about the N–O bond. For α a value close to the tetrahedral value 109° 28′ is expected; curves for α = 100, 105, 110, and 115° are shown.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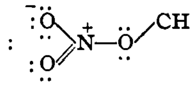
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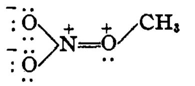
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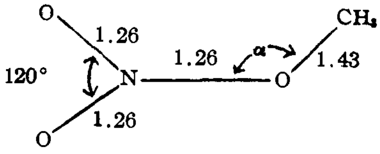

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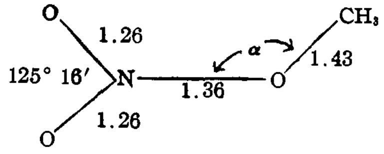

II

All of the curves show rough agreement with the photographs; the curves for model I are,

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(4) L. Pauling, L. O. Brockway and J. Y. Beach, THIS JOURNAL, 57, 2705 (1935).

however, all inferior to curve II–105° in regard to the observation of six well-shaped and nearly uniformly spaced rings. Curve II–105° is in nearly complete agreement with the experimental data, the greatest quantitative discrepancy, 3%, being shown by the fourth maximum (see Table II). We accordingly accept model II with α = 105° as supported by the electron diffraction data. The quantitative comparison verifies the interatomic distance values N–O = 1.36 Å. (for the oxygen atom with methyl attached), N–O = 1.26 Å. (for the other oxygen atoms), and O–C = 1.43 Å. to about ± 0.05 Å., the N–O–C bond angle being given the value 105 ± 5°. This configuration is compatible with the radial distribution curve (Fig. 1).

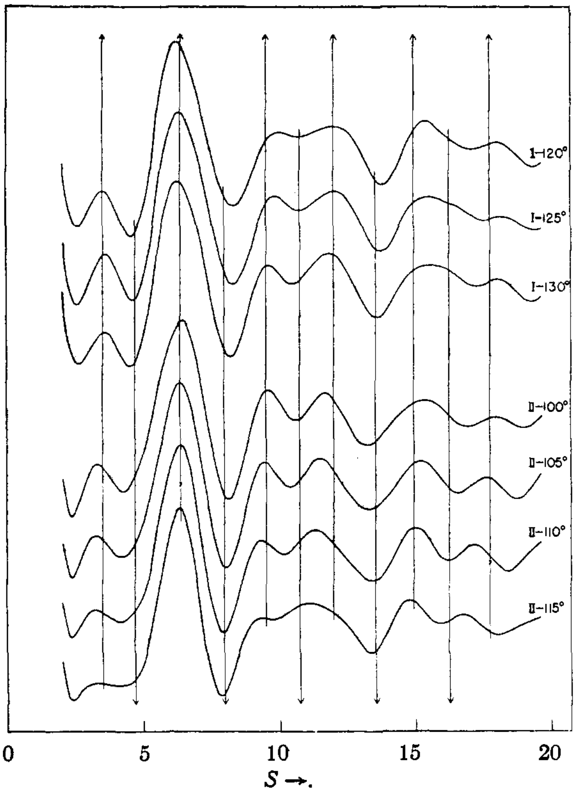

Fig. 3.—Intensity curves for methyl nitrate.

Fluorine Nitrate.—Fluorine nitrate, NO_3F, was first prepared by G. H. Cady[5] in 1934 by bubbling fluorine through dilute nitric acid. At the suggestion of Professor W. A. Noyes, we undertook the electron diffraction investigation of the vapor in order to determine where the fluorine atom is attached and what effect it has on the nature of the bonds in the NO_3 group. Professor D. M. Yost and Mr. A. Beerbower of these Laboratories[6] prepared samples of fluorine nitrate by Cady's method (using the original apparatus of Dr. Cady), and also by another method, consisting in passing fluorine over solid potassium nitrate, and kindly provided us with some of the substance for the electron diffraction work. The vapor of the substance at about 300 mm. pressure was held in a one-liter glass flask connected to the electron diffraction apparatus through an ordinary stopcock. The photographs obtained from the first sample showed four rings. An attempt to prepare heavier photographs from another sample was made unsuccessful by the explosion of the substance at the instant of making the first exposure. It was previously thought that fluorine nitrate gas was stable at room temperature, and the cause of the explosion is still unknown.

The s values and the visually estimated intensities for the four rings observed in the photographs are given in Table IV. The radial distribution function (Fig. 1) shows maxima at 1.27 and 2.29 Å., the second being about twice as large as the first.

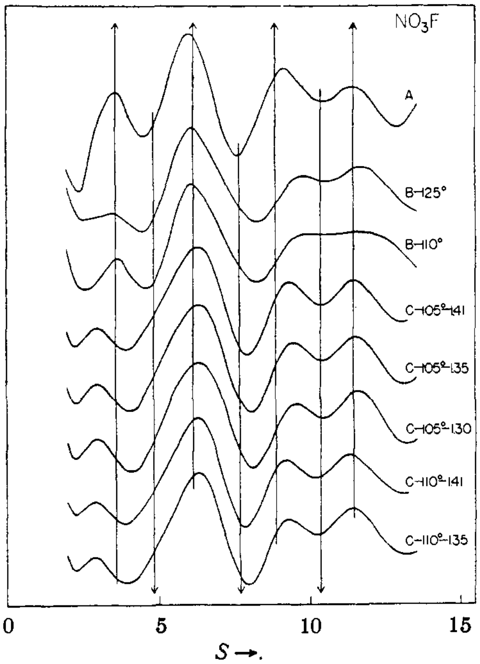

Fig. 4.—Intensity curves for fluorine nitrate.

The molecular models upon which the theoretical intensity curves of Fig. 4 are based have been chosen to distinguish between the three most probable configurations of fluorine nitrate. The

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(5) G. H. Cady, THIS JOURNAL, 56, 2635 (1934).

(6) D. M. Yost and A. Beerbower, *ibid.*, 57, 781 (1935).

first, suggested to us by Professor W. A. Noyes, involves a tetrahedral arrangement of the fluorine and oxygen atoms around the nitrogen atom, in which the bond angles are all 109° 28′ and the ratio of the N–F to the N–O distances is 0.985; the corresponding curve is marked A. The other two models are similar to those considered above for methyl nitrate. In the second (B) the double bond in the NO_3 groups is assumed to resonate equally among the three N–O bonds and the fluorine atom lies in the plane of the other atoms, with the interatomic distances as shown in Table III. In the third (C) the resonance of the double bond does not involve the oxygen atom to which the fluorine is attached (O′) but is restricted to the other two positions; with this structure the molecule is no longer coplanar but instead the NO′F plane is perpendicular to the NO_3 plane.

TABLE III

MODELS FOR NO_3F

Model	NO	NF	NO'	O'F	<ONO	<NO'F
A	1.40	1.38			109° 28′	
B–125°	1.26		1.26	1.34	120°	125°
B–110°	1.26		1.26	1.34	120°	110°
C–105°–1.41	1.26		1.36	1.41	125°	105°
C–105°–1.35	1.26		1.36	1.35	125°	105°
C–105°–1.30	1.26		1.36	1.30	125°	105°
C–110°–1.41	1.26		1.36	1.41	125°	110°
C–110°–1.35	1.26		1.36	1.35	125°	110°

The models for complete resonance, B, are eliminated because in the corresponding curves the third and fourth maxima are not well resolved from each other, as they are in the photographs. The remaining six curves are more satisfactory in this respect, the relative heights of the third and fourth maxima showing better agreement with the photographs for the curves A, C–105°–1.41, and C–105°–1.35 than for the other three.

TABLE IV

FLUORINE NITRATE

Max.	Min.	I	s, obsd.	s, calcd C–105° –1.41	s, calcd C–105° –1.35	s, calcd./s, obsd. C–105°– 1.41	s, calcd./s, obsd. C–105°– 1.35
1		2	3.56	2.95	2.97	(0.829)	(0.834)
	2		4.84	3.87	3.97	(0.800)	(0.821)
2		5	6.16	6.29	6.29	1.021	1.021
	3		7.66	7.89	8.04	1.030	1.050
3		2	8.88	9.34	9.46	1.052	1.065
	4		10.36	10.36	10.41	1.000	1.005
4		1	11.45	11.46	11.52	1.001	1.006
					Average	1.021	1.029
					N–O	1.286 Å.	1.296 Å.
					N–O′	1.389	1.400
					O–F	1.440	1.390

Model A cannot be eliminated definitely by the photographs; there are, however, some points which make this model improbable. From the curve for this model the first minimum would be expected to be at least as well pronounced as the second minimum, whereas on the photographs the first minimum is not very well defined. That the qualitative appearance of the photographs supports model C rather than model A is further shown by the fact that the photographs resemble those of methyl nitrate more closely than those of carbon tetrafluoride. Some evidence is also provided by the radial distribution curve (Fig. 1), the first peak being displaced by 0.15 Å. from the position expected for it for model A. For these reasons and the additional reason that it is difficult to correlate the tetrahedral configuration with an electronic structure involving only completed octets, we consider model A not to be satisfactory.[7]

The curves C–105°–1.41 and C–105°–1.35 are in reasonably good qualitative and quantitative agreement with the photographs, the discrepancies shown by the first maximum and second minimum being no larger than usual for inner rings. The quantitative comparison (Table IV) leads to the average interatomic distances N–O = 1.29 Å., N–O′ (with fluorine attached) = 1.39 Å., and O′–F = 1.42 Å., with probable errors of about ± 0.05 Å. The bond angles are O–N–O = 125 ± 5° and N–O′–F = 105 ± 5°. This configuration is compatible with the radial distribution curve (Fig. 1).

The Adjacent Charge Rule.—There are thus now known four substances (nitrous oxide, methyl azide, methyl nitrate, and fluorine nitrate) with configurations supporting the adjacent charge rule. That this rule is reasonable can be seen from the following argument. In general a valence-bond structure involving two charged atoms with opposite signs may correspond to about the same energy value as a structure involving uncharged atoms, the difference between the ionization energy of one atom and the electron affinity of the other being approximately compensated by the coulomb energy of the charges. For example, the coulomb interaction of the charges + *e* and − *e* 2.30 Å. apart stabilizes the structures $\overset{-}{:}\underset{\cdot\cdot}{\ddot{\mathrm{O}}}-\mathrm{C}\equiv\mathrm{O}\overset{+}{:}$ and $:\overset{+}{\mathrm{O}}\equiv\mathrm{C}-\underset{\cdot\cdot}{\ddot{\mathrm{O}}}\overset{-}{:}$ for carbon dioxide by 6.3 e. v., which

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(7) Quantitative comparison for this model leads to the interatomic distances N–O = 1.42 Å., N–F = 1.40 Å.

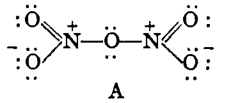
is roughly equal to the estimated energy required to remove an electron from one bound oxygen atom and attach it to another; it is accordingly not unreasonable that these two structures contribute about equally with the structure $:\ddot{O}=C=\ddot{O}:$ to the normal state of the molecule. For nitrous oxide the two structures $\bar{:}\ddot{N}=\overset{+}{N}=\ddot{O}:$ and $:N\equiv\overset{+}{N}-\ddot{O}\bar{:}$ have nearly equal covalent bond energies and coulomb energies and would be expected to make about equal contributions. The structure $\bar{:}\underset{\cdot\cdot}{\ddot{N}}-\overset{+}{N}\equiv\overset{+}{O}:$, however, with adjacent positive charges adding a large positive quantity to the energy of the molecule, corresponds to a higher energy value than the other two structures, and accordingly makes no significant contribution to the normal state of the molecule.

The principal application of the adjacent charge rule is to the compounds of nitrogen. In many compounds a nitrogen atom forms four covalent bonds and has a positive charge; the adjacent charge rule then prevents resonance to structures in which an atom attached to this nitrogen atom also has a positive charge. The covalent azides and nitrates are the principal substances of this type. It is interesting to note that the adjacent charge rule provides an explanation of the large differences in stability shown by covalent and ionic azides and nitrates. Covalent azides and nitrates are restricted by the rule to resonance between two important structures, whereas the ions resonate among three structures. The resonance energy[8] for two structures is about 1 e. v. and for three structures about 2 e. v.; hence ionic azides and nitrates are more stable than the covalent substances by about 25,000 cal. per mole. We accordingly understand why the alkali and alkaline earth azides[9] can be exploded only at high temperatures whereas the heavy metal azides, chlorazide, cyanuric triazide, and other covalent azides are extremely explosive. Similarly the ionic nitrates are relatively stable, whereas the covalent nitrates (methyl nitrate, nitroglycerine, etc.) are exploded easily. It may be pointed out that the covalent nitrates are more closely related to nitro compounds than to the nitrate ion from the resonance point of view, in that in covalent nitrates, as in nitro compounds, the double bond resonates between two oxygen molecules, whereas in the nitrate ion it resonates among three.

The destabilizing effect of the adjacent charge rule shown in covalent nitrates does not occur in the analogous compounds containing carbon as the central atom, such as carbonates, urea, guanidine, etc., since the quadricovalent carbon atom is neutral.

The question as to whether or not hydrazoic acid and nitric acid are more closely related to the corresponding covalent compounds than to the ions could be answered by determining the configurations of the acids. From general information we would predict that the H–N and H–O bonds are essentially covalent (with perhaps about one-third ionic character) and that the N_3 and NO_3 groups in the acids have the same structures as in methyl azide and nitrates. This prediction is supported by the instability of the acids.

The adjacent charge rule permits resonance of nitrogen pentoxide among the four structures of type A, but excludes the four structures of type B (as well as the structure with two double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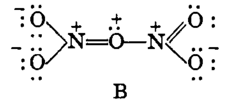
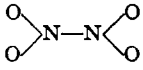
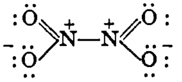

B

bonds to the central oxygen atom). We accordingly predict for the molecule a configuration in which the two interatomic distances N–O′ (O′ being the central oxygen atom) have about the single-bond value 1.36 Å. and the four distances N–O have about the double-bond value 1.26 Å., each NO_3 group being coplanar, with the angles ONO equal to about 125° and NO′N to about 110°; the relative orientation of the two NO_3 planes is uncertain, since the single N–O′ bonds permit free rotation.[10]

The symmetrical configuration  is usually assumed for nitrogen tetroxide.[11] However, the only reasonable electronic structures involving completed octets which can be written for this configuration are the four of the type  which are incompatible with

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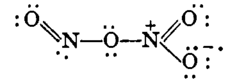
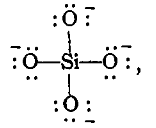
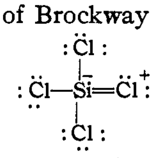
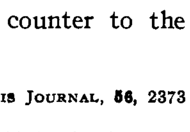
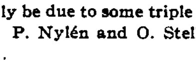
[8] L. Pauling and J. Sherman, *J. Chem. Phys.*, **1**, 606 (1933).

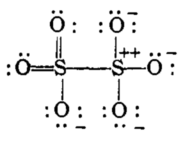
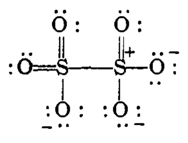
[9] The alkali azides are known to be ionic: S. B. Hendricks and L. Pauling, THIS JOURNAL, **47**, 2904 (1925); L. K. Frevel, *ibid.*, **58**, 779 (1936).

(10) L. R. Maxwell, V. M. Mosley and L. S. Deming, *J. Chem. Phys.*, **2**, 331 (1934), report the values N–O = 1.18 Å. and N–O′ = 1.3–1.4 Å. on the basis of electron diffraction data, in agreement with our structure.

(11) S. B. Hendricks, *Z. Physik*, **70**, 699 (1931); G. B. B. M. Sutherland, *Proc. Roy. Soc.* (London), **A141**, 342, 535 (1933); Maxwell, Mosley and Deming, ref. 10; L. Harris and G. W. King, *J. Chem. Phys.*, **2**, 51 (1934).

the adjacent charge rule. We accordingly believe that nitrogen tetroxide has not this configuration but instead the unsymmetrical configuration corresponding to resonance between the two structures of type .

The adjacent charge rule provides some information regarding the nature of the bonds in the oxygen acids of heavier atoms. It has become customary, following Lewis, to assign to the silicate ion and related groups structures such as , the octet rule being considered to hold for the heavier atoms as well as for the first-row atoms. The discovery of Brockway and Wall[12] that structures such as  are important for silicon tetrachloride and other halides of non-first-row atoms suggests that corresponding structures might be important for the oxygen compounds also. Strong support for this idea is provided by the observed interatomic distances in crystals, as determined by W. L. Bragg, Zachariasen, and others, which are approximately equal to the sums of double-bond radii (Table V), indicating strong resonance to structures involving double bonds.[13] Dithionic acid, $H_2S_2O_6$, and hypophosphoric acid, $H_4P_2O_6$, are stable substances, resisting oxidation even by dichromate.[14] This stability would not be expected for the completed octet structures  and , which run counter to the adjacent charge rule; the rule instead requires us to accept as the important structures for these substances those in which a sulfur atom forms two double bonds and a phosphorus atom one double bond, such as

 ,  etc., and

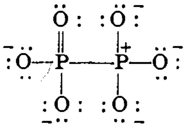
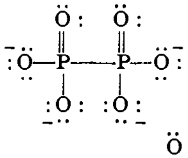
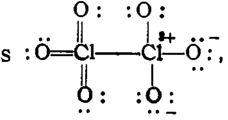
 ,  etc.

TABLE V

INTERATOMIC DISTANCES M–O IN IONS MO_4

	SiO_4^{4-}, Å.	PO_4^{3-}, Å.	$SO_4^{=}$ Å.	ClO_4^-, Å.
Observed values	1.60	1.53	1.50	1.48
Sums of single-bond radii	1.83	1.76	1.70	1.65
Sums of double-bond radii	1.65	1.58	1.53	1.48

For Cl_2O_6 structures such as , etc., are allowed by the adjacent charge rule. We consider it probable that the dissociation of this substance is due not to its instability (weakness of the Cl–Cl bond) but instead to the unusual stability of the odd molecule ClO_3 through three-electron bond formation, as in the other odd molecules NO_2, NO, ClO_2, etc. It is possible that Cl_2O_6 has an unsymmetrical configuration, O_3Cl–O–ClO_2, analogous to that which we have suggested for N_2O_4; however, chlorine, unlike nitrogen, has more than four orbitals in its outer shell and hence the adjacent charge rule does not eliminate the symmetrical configuration, which we consider to be the more likely one because of analogy with the dithionate and hypophosphate ions.

We wish to thank Dr. G. H. Cady for lending us his apparatus, Professor Don M. Yost and Mr. A. Beerbower for preparing the fluorine nitrate used in this work, Mr. K. S. Palmer for assisting in the preparation of the electron diffraction photographs, and Dr. Sidney Weinbaum and Mrs. M. Lassettre for assisting in their interpretation.

Summary

The investigation of methyl azide, methyl nitrate, and fluorine nitrate by electron diffraction is shown to lead to configurations of the molecules corresponding in each case to resonance between two important valence-bond structures. The unimportance of a third otherwise reasonable structure for these molecules as well as for nitrous oxide is ascribed to instability due to the presence of electric charges of the same sign on adjacent atoms. It is shown that the differ-

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[12] L. O. Brockway and F. T. Wall, THIS JOURNAL, 56, 2373 (1934).

[13] The observed decrease below the double-bond values may possibly be due to some triple bond formation.

[14] P. Nylén and O. Stelling, *Z. anorg. allgem. Chem.*, 212, 169 (1933).

ences in chemical properties of covalent and ionic azides and nitrates can be correlated with differences in structure. The use of the adjacent charge rule is illustrated by its application in the discussion of the structures of nitrogen pentoxide, nitrogen tetroxide, and the oxygen acids of heavier atoms.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENTS OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES AND THE CALIFORNIA INSTITUTE OF TECHNOLOGY]

The Reaction between Osmium Tetroxide and Hydrobromic Acid. II. Rate Study

BY H. DARWIN KIRSCHMAN AND WILLIAM R. CROWELL[1]

In a previous article on a study of the equilibrium between osmium tetroxide, hydrogen ion and bromide ion at 100°, it was suggested that at low acid and high bromine concentrations the reaction might be of the type[2]

$$OsO_4 + H^+ + {}^5/_2Br^- \rightleftharpoons Os(OH)O_3{}^-Br + {}^1/_2Br_3{}^- \quad (1)$$

The purpose of the present work was to carry out a study of the rate of the reaction between osmium tetroxide, hydrogen ion and bromide ion with a view of learning more of its nature and to determine, if possible, the validity of certain assumptions made in the earlier investigation.

The general plan of the work consisted of the analysis for bromine of the contents of the reaction tubes at various time intervals in experiments conducted in a manner similar to that employed in the equilibrium problem. From the results obtained an attempt was made to determine the order of the reaction with respect to octavalent osmium, hydrogen ion and bromide ion.

The general form of the rate expression can be stated as

$$-\frac{d(OsO_4)}{dt} = k(Os_8)^a\,(H^+)^b\,(Br^-)^c\,\frac{(f_1)^a\,(f_2)^b\,(f_3)^c}{f_4}$$

In the present instance $k = k_0K$ where k_0 is the specific reaction rate constant and K the equilibrium constant of the intermediate complex. f_1, f_2, f_3 and f_4 are the activity coefficients of octavalent osmium, hydrogen ion, bromide ion and the intermediate complex, respectively.

In the first series of experiments, the initial concentration of all the reacting constituents was kept constant except that of the osmium, which was changed about twofold. A second series of runs was made at different concentrations of hydrobromic acid but at a fixed initial concentration of osmium. A third series of runs was made at approximately constant ionic strength and at the same initial concentration of octavalent osmium. Some of these runs were carried out at different concentrations of bromide ion but at a fixed concentration of hydrogen ion. In other runs the bromide ion concentration remained constant while the hydrogen ion concentration was changed. The purpose of the experiments at constant ionic strength was to determine the orders with respect to hydrogen and bromide ion, and to see if the sum of these orders was approximately equal to the order with respect to hydrobromic acid found in the second series of runs. Finally, using the rate data thus obtained, a series of rate constants was calculated.

Experimental

The apparatus was that employed in the equilibrium experiments.[2] The potassium hydroxide solution of osmium tetroxide was prepared as described in our previous article on the determination of octavalent osmium.[3] The hydrobromic acid was prepared from red phosphorus and bromine by the well known method. The middle fraction of the distillate was redistilled until a water white product was obtained.

The experimental procedure was essentially the same as that used in the equilibrium experiments with one modification in the case of the solutions 1.2 and 1.6 *M* in hydrobromic acid. In these solutions there was a tendency for the bromine formed to react with the reduced osmium when the tubes were broken in the chilled water in the titration beaker. To overcome this difficulty, sufficient hydrobromic acid was added to the water in the titration beaker to make the acid concentration after the addition of the contents of the reaction tube about 0.1 *N*.

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(1) The authors were assisted in the experimental work by Messrs. Glen Seaborg and Robert Brinton, students in the Chemistry Department at the University of California at Los Angeles.

(2) Kirschman and Crowell, THIS JOURNAL, **55**, 488 (1933).

(3) Crowell and Kirschman, *ibid.*, **51**, 175 (1929).