936. *Oxides and Oxy-ions of the Non-metals. Part IV.* Nitrogen Derivatives.*

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Electron-spin resonance data for radicals trapped in irradiated nitrates and alkali halides doped with nitrogen oxides and oxy-ions [1,2] are re-interpreted in terms of the species NO_2, NO_2^{2-}, NO_3, and NO_3^{2-}. The data are compared with those of isoelectronic radicals.

ALTHOUGH the effect of high-energy radiation on metal nitrates and nitrites has been studied extensively [1-3] it is only recently that a firm identification of one of the resulting paramagnetic centres as nitrogen dioxide has been achieved by electron-spin resonance methods.[4,5] Recently, results for a variety of radicals formed by irradiation of alkali halide crystals doped with certain oxy-ions of nitrogen have been published and interpreted.[6] Also, spin-resonance data for irradiated potassium nitrate crystals have been described and attributed to similar centres.[1,7] Results for nitrogen dioxide can thus be used as a measure by which to gauge data for centres in other crystals that might be expected to contain the trapped dioxide after irradiation.

Results are now known for several oxy-radicals of non-metals with which those thought to be due to corresponding oxy-radicals of nitrogen should be compared. Thus, data assigned to NO_3^{2-} should be compared with those for the groups PO_3^{2-},[8] SO_3^-,[9] and ClO_3,[10,11] and those assigned to NO_2^{2-} should be compared with *g*-tensors derived for O_3^-,[10] SO_2^-,[12] and ClO_2 [10,13] and with the hyperfine coupling tensor for ClO_2.[13]

Furthermore, since the energy-level schemes of Mulliken [14] and Walsh [15] have been so well supported by electron-spin resonance data, they can be used with considerable confidence to predict results for radicals other than those already mentioned.

In the following we give reasons for preferring the assignments given in Table 1, and in the discussion we compare our conclusions with those of others.[1,6,7,16,17]

Nitrogen Dioxide.—It is surprising that none of the results for doped alkali halides [6] corresponds directly with those expected for nitrogen dioxide [5] since it is highly probable that this radical is formed under the conditions used. However, we tentatively ascribe the results labelled 3 in Table 1 to this dioxide. These should be compared with those estimated for nitrogen dioxide rotating in the *xy* plane (radical 2a of Table 1). Values for g_{av} and A_{iso} are in satisfactory agreement, and the magnitude of the anisotropic hyperfine coupling tensor is very close to that expected for dioxide. However, the sign of this tensor is wrong. The data may relate to another radical which fortuitously has parameters close to those expected for nitrogen dioxide. The latter alternative is hard to accommodate since the only other radical likely to have a large isotropic coupling to ^{14}N

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* Part III, preceding paper.

[1] Cunningham, Symposium on Free Radicals, Uppsala, 1961, p. 13-1.
[2] Bleaney, Hayes, and Llewellyn, *Nature*, 1957, **179**, 140.
[3] Cunningham and Heal, *Trans. Faradav Soc.*, 1958, **54**, 1355.
[4] Atkins, Keen, and Symons, *J.*, 1962, 2873.
[5] Zeldes and Livingston, *J. Chem. Phys.*, 1961, **35**, 563.
[6] Jaccard, *Phys. Rev.*, 1961, **124**, 60.
[7] Cunningham, McMillan, Smaller, and Yasaitis, *Phys. and Chem. Solids*, 1962, **23**, 167.
[8] Horsfield, Morton, and Whiffen, *Mol. Phys.*, 1961, **4**, 473.
[9] Chantry, Horsfield, Morton, Rowlands, and Whiffen, unpublished work.
[10] Atkins, Brivati, Keen, Symons, and Trevalion, preceding paper.
[11] Cole, *J. Chem. Phys.*, 1961, **35**, 1169.
[12] Clark, Horsfield, and Symons, *J.*, 1961, 7.
[13] Cole, *Proc. Nat. Acad. Sci. U.S.A.*, 1960, **46**, 506.
[14] Mulliken, *Rev. Mod. Phys.*, 1942, **14**, 204.
[15] Walsh, *J.*, 1953, 2266.
[16] Schoemaker and Boesman, *Compt. rend.*, 1961, **252**, 2099.
[17] Boesman and Schoemaker, *Compt. rend.*, 1961, **252**, 2865.

TABLE 1.

Data for oxides and oxy-ions of nitrogen.

For NO_2 and NO_2^{2-} the *x*-axis is perpendicular to the molecular plane. The *z*-axis bisects the ONO angle. For NO_3 and NO_3^{2-} the *z*-axis is the C_{3v} symmetry axis.

			Hyperfine splitting (gauss)								
			anisotropic			isotropic					
Suggested species	No.	Medium	A_{xx}	A_{yy}	A_{zz}	A_{iso}	g_{xx}	g_{yy}	g_{zz}	g_{av}	Ref.
NO_2	1	H_2O	−6·28	−7·04	13·33	56·88	2·0066	1·9920	2·0022	2·0003	4
	2	$NaNO_2$	−5·27	−7·95	13·22	54·71	2·0057	1·9910	2·0015	1·9994	5
	2a ‡		−6·61	−6·61	13·22	54·71	1·9983	1·9983	2·0015	1·9994	—
	2b ‡		3·97	−7·95	3·97	54·71	2·0036	1·9910	2·0036	1·9994	—
	2c ‡		−5·27	2·63	2·63	54·71	2·0057	1·9962	1·9962	1·9994	—
	3	KCl *	6·4	6·4	−12·9	56·1	2·0003	2·0003	2·0014	2·0007	6
	4	$Pb(NO_3)_2$	−4·7	2·3	2·3	54·7	2·004	1·995	1·995	1·998	§
NO_2^{2-} ...	5	KCl *	−7·3	−9·3	16·6	14·3	2·0070	2·0099	2·0038	2·0069	6
	6	KCl †				13·7				2·0069	16
	7	KNO_3	−9·5	−9·5	19·0	13·0	2·008	2·010	2·004	2·007	1
NO_3	8	KNO_3	0	0	0	4·5	2·025	2·025	2·005	2·018	1
	9	$Pb(NO_3)_2$	−0·7	−0·7	1·3	1·7	2·029	2·029	1·998	2·019	§
NO_3^{2-} ...	10	KCl *	−10·3	−10·3	20·7	40·8	2·0068	2·0068	2·0020	2·0052	6
	11	KCl †				39·5				2·0045	17
	12	KNO_3	−9·7	−9·7	19·3	41·7	2·006	2·006	2·002	2·005	1

* Similar values are found in KBr and KI. † Similar values are found in KBr and NaCl.
‡ 2a, b, and c refer to NO_2 undergoing rotation restricted to the *xy*, *xz*, and *yz* planes, respectively.
§ Golding, Henchman, and Longuet-Higgins, personal communication.

is NO_3^{2-}: this would have to rotate in the *xz* or *yz* plane to give the observed results, which seems the least probable mode of rotation. Also, if the results discussed below are correctly assigned to NO_3^{2-}, then this alternative can hardly be justified unless a grossly different environment is involved. The constancy of the data assigned to NO_3^{2-} in different environments augurs against this.

The concept of such rotation restricted to one plane has been considered [4] for nitrogen dioxide trapped in solid argon.[18] The experimental results [18] correspond closely to the calculated values given in Table 1 (no. 2b). Similarly, results for a radical trapped in irradiated lead nitrate correspond closely to those calculated for nitrogen dioxide rotating in the molecular plane (2c) which is the plane of the parent nitrate ion.

The Radical NO_2^{2-}.—Our assignment (Table 1) rests on the following arguments. The radical is expected to have an unpaired electron in a b_1 orbital which can be constructed by out-of-phase overlap of the three p_x orbitals. Thus the greatest hyperfine coupling should occur for the field in the *x*-direction, as is found. The isotropic coupling should be small and positive, the value, between 14 and 15 gauss, being close to those for several radicals with similar electronic configuration.[19]

Also, the *g*-values are in good accord with expectation, being comparable with those for the isoelectronic radical O_3^-,[10] which has $g_x = 2·0025$, $g_y = 2·0174$, $g_z = 2·0113$, and $g_{av} = 2·0104$.

Cunningham [1] found that at 4°K three values were obtained, repeating every 120° in the nitrate plane. This can be understood if NO_2^{2-} is formed in a nitrate site by arbitrary loss of any of the three oxygens, followed by electron-capture by the resulting oriented nitrite ions. On warming to 77°K, these radicals became equivalent, presumably owing to rotation within the plane.

These results were assigned to nitric oxide by Cunningham [1] and by Jaccard,[6] and to the dioxide by Schoemaker and Boesman.[16]

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[18] Jen, Foner, Cochran, and Bowers, *Phys. Rev.*, 1958, **112**, 1169.

[19] Symons, "Inorganic Free Radicals," ed. R. F. Gould, A.C.S. Monograph, 1962 (Advances in Chemistry Series).

Nitrogen Trioxide.—Although results for similar radicals are not yet known, it is possible to predict data rather precisely for this radical since it is formed by loss of one electron from the nitrate ion, whose electronic structure is well understood.[15,20] Thus NO_3 should be planar, and to a good first approximation the unpaired electron should be in a non-bonding π-level entirely on oxygen. Anisotropic interaction between this electron on oxygen and the nitrogen nucleus should be very small, probably contributing less than 0·5 gauss to the total coupling. Configurational interaction will mix in excited states which will contribute to the isotropic nitrogen hyperfine coupling, but this will be small and should not exceed a few gauss.

The g-tensor should have axial symmetry with $g_{/\!/}$ along the molecular axis tending to the free-spin value (2·0023) and $g_{\perp}$ considerably greater than this, since coupling is expected to occur primarily with filled levels on oxygen.

These expectations are well fulfilled for a radical detected in irradiated nitrate by Cunningham[1] (no. 8 in Table 1), except that the hyperfine coupling is stated to be isotropic. Since the unpaired electron is in a degenerate e-level a considerable Jahn–Teller distortion is expected. This will be reflected primarily in the g-tensor and is not likely to reduce the anisotropic hyperfine coupling to ^{14}N to zero.

These results were assigned to the radical-ion NO_3^{2-} by Cunningham.[1]

The Radical NO_3^{2-}.—In contrast with NO_3, here the odd electron should be in a level largely confined to nitrogen. However, just as linear 16-electron dioxides bend when accommodating an extra electron, so planar nitrate ions are likely to become pyramidal. This tendency will be strongly opposed by steric interactions between non-bonding electrons on oxygen; so deviation from the planar configuration may be small, and should be considerably less than for PO_3^{2-}. Thus the $\angle$ONO angle should lie between 120° and 110° which is thought to be the $\angle$OPO angle in PO_3^{2-}.[8] Alternatively, one could say that the $p : s$ ratio should be greater for NO_3^{2-} than PO_3^{2-}.

The g-tensor should have axial symmetry, with g_z close to the free-spin value and with g_x and g_y equal and somewhat greater than g_z.

All these expectations are fulfilled in the data for radicals nos. 10, 11, and 13 of Table 1. This is Jaccard's conclusion, but Cunningham[1] suggested NO_2^{2-} for this species, and Boesman and Schoemaker[17] postulated NO_3.

Our expectation that NO_3^{2-} would be nearly planar is borne out by these data, and we calculate a bond angle of 116° from the $p : s$ ratio of 9·5, and the relationships described by Coulson.[21] This represents a deviation of about 13° from planarity. The contrast with electronically similar oxides of second-row elements is most marked, and it is related to the fact that, in contrast with phosphorus, orthonitrites are unknown and orthonitrates (NO_4^{3-}) are very rarely formed[22] and readily revert to ordinary nitrates. However, the difference between NO_3^{2-} and PO_3^{2-} is not completely established since, if phosphorus d-levels are important components of the a_1 level in PO_3^{2-}, then the estimated bond angle could be smaller than the true value.

Discussion.—Our approach to identification differs from that of others[1,6,7,16,17] in that we assume that the predictable electronic levels for di- and tri-oxides will not be so modified by intermolecular forces that well-separated levels are inverted. Jaccard,[6] on the other hand, gauged the nature of the centres primarily by their tendency to grow or decay when electrons were released into the crystal by optical bleaching of F-centres, or when " holes " from $(Hal)_2^-$ centres were liberated on warming. Cunningham[1] invoked Jaccard's results in part, and also information from optical spectroscopy. Our calculations are given in Table 2.

The argument based upon electron gain or loss is a difficult one to apply unless there is

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[20] Friend and Lyons, *J.*, 1959, 1572.

[21] Coulson, " Victor Henri Volume Commemoratif, Contribution a l'Étude de la Structure Moleculaire," Defoer, Liège, 1948, p. 15.

[22] Kohlmuller, *Ann. Chim.* (*France*), 1959, **4**, 1183.

certainty regarding the nature of the original species. Thus, if nitrite reacts with liberated electrons, NO_2^{2-} will be formed, but if, for example, NO_2^+ is present, then NO_2 will result. Since all that is known for doped alkali halides is that species giving rise to detectable spin-resonance absorption are not initially incorporated, many of the detailed arguments in favour of a given species are insecurely based.

Both Jaccard and Cunningham suggest that the radical we identify as NO_2^{2-} is nitric oxide. It is not possible to disprove this contention, since the magnetic properties of linear molecules are markedly dependent upon environment and hence hard to predict. Indeed, it seems remarkable, if this centre is nitric oxide, that its properties are almost the same in various alkali halide lattices and also in potassium nitrate. The major weakness in the postulate is that the unpaired electron in nitric oxide, which is normally in a π^*-level, must be constrained by the crystal field to occupy a σ^*-level. Jaccard [6] proposed that the π^*-level is raised above the σ^*-level by the field from neighbouring halide ions: this we find hard to accept, especially for the freely rotating oxide.

TABLE 2.

Calculated parameters for oxides and oxy-ions of nitrogen.

a_s^2 and a_p^2 are the electron population of the nitrogen 2*s*- and 2*p*-orbitals, respectively; a_o^2 gives the amount of electron on oxygen; and $\lambda^2 = a_p^2/a_s^2$.

Species	NO_2				NO_2^{2-}			NO_3		NO_3^{2-}		
No.	1	2	3	4	5	6	7	8	9	10	11	12
a_s^2	0·107	0·103	0·106	0·103	0·027	0·026	0·024	0·008	0·003	0·077	0·074	0·079
a_{px}^2	0·019	0·054										
a_{pz}^2	0·452	0·471	0·460		0·591		0·677		0·046	0·737		0·688
a_o^2	0·45	0·43	0·43		0·41		0·32					
λ^2	4·26	4·50	4·34							9·57		8·71
$<$ONO	134°	134°	134°							116°		115°

The radical that we describe as NO_3^{2-} is thought by Cunningham [1] to be NO_2^{2-} since irradiated potassium nitrate containing this species had an absorption band at 355 mμ. It seems probable that this band is a property of nitrite ions which are undoubtedly a major reaction product [3] and have a characteristic absorption band in this region. It is hard to see why NO_2^{2-} should have considerable 2*s*-character in the unpaired electron's orbital.

Conclusions.—It seems probable that the tabulated results are correctly assigned to the radicals NO_2^{2-}, NO_3, and NO_3^{2-}. We are far less certain about the identity of radical no. 3, for reasons given above, and suggest that, in doped alkali halides, the situation may be complicated by chemical interactions similar to those found for electron-deficit centres.[23]

For example, the equilibria, $NO + Cl^- \rightleftharpoons NOCl^-$, and $NO_2 + Cl^- \rightleftharpoons NO_2Cl^-$, ought to be considered. If chlorine is attached to nitrogen these new radicals resemble NO_2^{2-} and NO_3^{2-}, respectively, and might be expected to have somewhat similar properties. However, one would expect to see hyperfine splitting from chlorine nuclei, at least for certain orientations of the radicals.

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[23] Symons and Doyle, *Quart. Rev.*, 1960, **14**, 62.