

561. Oxides and Oxyions of the Non-metals. Part II.
CO₂⁻ and NO₂.

By P. W. ATKINS, N. KEEN, and M. C. R. SYMONS.

Spectrophotometric and magnetic data for the radical-ion CO₂⁻ formed in crystalline formates are presented and compared with those for the isoelectronic nitrogen dioxide. The major feature of the results, which are in good accord with expectation for the normally accepted structure of these species, is that the unpaired electron is considerably more delocalised on to oxygen in nitrogen dioxide than in CO₂⁻.

The significance of hyperfine coupling with alkali-metal cations, which is a notable feature of the electron-spin resonance spectra, is also discussed.

THE conclusion drawn simultaneously by Ovenall and Whiffen¹ and by Brivati *et al.*,² that exposure of certain crystalline alkali-metal formates to γ -radiation resulted in the formation and trapping of CO₂⁻ radical-ions, has been further substantiated by Ovenall and Whiffen,³ whose analysis of the data from electron-spin resonance measurements shows them to be consistent with expectation, and yields, in particular, a bond angle of 134° which is identical with that for isoelectronic nitrogen dioxide. Our results for sodium formate, mentioned earlier,² are almost identical with theirs and are not further described.

In the expectation that the treatment of Ovenall and Whiffen³ would prove satisfactory for analysis of the spin-resonance spectrum of nitrogen dioxide, and because a comparison of results should be of interest, we undertook to determine the hyperfine coupling and *g*-tensors for this molecule: published results did not appear to be satisfactory (see Table 3). In particular, the results for the isotropic component of the hyperfine coupling to ¹⁴N derived from a solution of nitrogen dioxide in carbon tetrachloride⁴ is far larger than one might expect: and results of McDowell and his co-workers⁵ on nitrogen dioxide trapped in various rare-gas matrixes at 4°K give an isotropic splitting of about half this value, which is well in accord with Zeldes and Livingston's recent results⁶ for a radical, thought to be nitrogen dioxide, trapped in irradiated single crystals of sodium nitrite. Our own results with nitrogen dioxide trapped in media such that rotation is totally or largely prevented are in good accord with those for the radical described by Zeldes and Livingston⁶ and confirm their tentative conclusion that this is nitrogen dioxide. Because their data⁶ are more precise than those derived from radicals dispersed randomly, we have used them⁶ in preference to ours when discussing electronic structure.

¹ Ovenall and Whiffen, *Proc. Chem. Soc.*, 1960, 420.

² Brivati, Keen, Symons, and Trealion, *Proc. Chem. Soc.*, 1961, 66.

³ Ovenall and Whiffen, *Mol. Phys.*, 1961, 4, 135.

⁴ Bird, Baird, and Williams, *J. Chem. Phys.*, 1958, 28, 738.

⁵ Farmer, Hutchinson, and McDowell, Fifth Internat. Symposium on Free Radicals, Uppsala, 1961, 44-1.

⁶ Zeldes and Livingston, *J. Chem. Phys.*, 1961, 35, 563.

EXPERIMENTAL AND RESULTS

Materials.—Formates and oxalates were used as powders or grown as single crystals from aqueous solution.

Nitrogen dioxide, prepared from hot, dry lead nitrate was passed over phosphoric oxide in a stream of dry oxygen and collected as dinitrogen tetroxide at -80° . It was also prepared in solid nitromethane, and in a freshly prepared solid solution of dinitrogen tetroxide in water, by irradiation at 77°K with ultraviolet light from a medium-pressure mercury arc.

γ -Radiation.—Crystals and powders were exposed to γ -rays from a ^{137}Cs source at room temperature.³ Radical yields from oxalates were very low relative to those from formates.

TABLE 1.

Details of electron-spin resonance spectra obtained from polycrystalline formates and oxalates after exposure to γ -rays.

Compound	ΔH_{MS}^a (gauss)	g value ^b	No. of pronounced features	Other relevant details of the spectrum
<i>Formates</i>				
NH ₄	11	1.9992	1	Shoulder on high field side
Ba	24	2.0020	3	See Fig. 1
Cd	24.5	1.9986	4	
Ca	25.5	2.0004	4	2 cross-over points
		2.0059		
Li, H ₂ O	14	1.9998	1	Isotropic hyperfine coupling from $^7\text{Li} < 4$ gauss
Mg, 2H ₂ O	11	2.0017	2	Shoulder on high-field side
K	24	2.0048	4	Isotropic hyperfine coupling from $^{39}\text{K} = 7.0$ gauss
Na	34.5 ^c	2.0010	4	Isotropic hyperfine coupling from $^{23}\text{Na} = 8.2$ gauss
Zn	25	2.0003	4	
<i>Oxalates</i>				
Al, H ₂ O	19	2.0014	1	
(NH ₄) ₂ , H ₂ O ...	24	2.0004	3	2 shoulders on low-field side
Cd	19	2.0002	3	Sharp line with shoulders on both sides
Ca, H ₂ O	25	1.9996	4	
Li ₂	14	2.0017	1	Broadening on high-field side
Mg	10.5	2.0011	2	Shoulder on high-field side
K ₂ , H ₂ O	24	1.9996	3	2 small shoulders on low-field side
Na ₂	18	2.0031	2	Shoulder on high-field side
Zn, H ₂ O	24	2.0022	4	
NH ₄ H	6	2.0043	1	Broadening on high-field side
KH	4	2.0053	1	Sharp line with shoulders on both sides
NaH	10.5	2.0015	2	1 : 1 doublet, broader on high-field side; splitting ~ 6 gauss
H ₂ C ₂ O ₄ , 2H ₂ O ...	29	—	5	Sharp central line with 2 shoulders on either side

^a Distance between extreme "pronounced features" on the derivative curve, measured from appropriate maxima and minima. ^b g -Value measured at the main cross-over point on the derivative curve. ^c 37 at 77°K .

Electron-spin Resonance.—Spectra were measured at 3 cm. by a high-resolution spectrometer described previously.⁷

Single crystals were mounted on Perspex rods inserted in the rectangular cavity and rotated externally about an axis perpendicular to the magnetic field. Results for sodium formate were closely similar to those of Ovenall and Whiffen.³ Those for other formates and oxalates are summarised in Table 1, and a typical spectrum is given in Fig. 1. In several instances, single crystals were studied in various orientations, but apart from those for alkali-metal formates, the results have defied interpretation. Certainly, CO_2^- is not the only radical detected. A spin-resonance spectrum for nitrogen dioxide trapped in ice at 77°K is shown in Fig. 2, and the results obtained therefrom are given in Table 3, together with those of other workers for this molecule. In deriving the magnitudes of the hyperfine and g -tensors from this spectrum we have used the procedure outlined by Kneubühl:⁸ the three peaks are

⁷ Brivati, Keen, and Symons, *J.*, 1962, 237.

⁸ Kneubühl, *J. Chem. Phys.*, 1960, **33**, 1074.

TABLE 2.

Details of diffuse reflectance spectra ($m\mu$) of γ -irradiated formates and oxalates.

Salt	1st band (weak)	2nd band (intense)	3rd band (intense)
HCO ₂ Na	340	280	255
Mg(HCO ₂) ₂ ·2H ₂ O	340	300	255
Ca(HCO ₂) ₂	340 ^a	280	250
Ba(HCO ₂) ₂	335 ^a	275	255
Zn(HCO ₂) ₂	340 ^a	275	260
Cd(HCO ₂) ₂	345 ^{a, b}	275	260
Na ₂ C ₂ O ₄	—	—	255 ^c
CaC ₂ O ₄ ·H ₂ O	—	—	255 ^c

^a Poorly defined shoulder. ^b Marked absorption also in 400 $m\mu$ region. ^c This band is found in unirradiated oxalates.

TABLE 3.

Experimental results for nitrogen dioxide.

Source	Medium	g -Values				Hyperfine interaction (gauss)			
		g_x	g_y	g_z	g_{av}	A_x	A_y	A_z	A_{iso}
Present work	Ice (77° K)	2.0066	1.9920	2.0022	2.0003	-6.28	-7.04	13.33	56.88
Zeldes <i>et al.</i> ⁶	NaNO ₂	2.0057	1.9910	2.0015	1.9994	-5.27	-7.95	13.22	54.71
		± 0.0005	± 0.0005	± 0.0005					
Jen <i>et al.</i> ^{17, a}	Argon	2.0037 ^b	1.990	2.0037 ^b	1.9991	3.6 ^b	-7.2	3.6 ^b	54.2
Farmer <i>et al.</i> ⁵	Argon				2.0005				54.60
Bird <i>et al.</i> ⁴	CCl ₄				2.008 \pm 3				107.6
Bleaney <i>et al.</i> ^c	La ₂ Mg ₃ (NO ₃) ₁₂ ·24H ₂ O	2.005	1.994	2.004	2.001	0.36	-7.14	6.78	60.7
		± 0.002	± 0.002	± 0.002	± 0.002				

^a Our interpretation. ^b Averages; see text. ^c Bleaney, Hayes, and Llewellyn, *Nature* 1957, 179, 140.

associated together and give one g -value and hyperfine splitting: the two sets of shoulders, which are identified unambiguously by the requirement that the splitting between individual lines be a constant, give the other g -values and splittings. These have been compared with the results of Zeldes and Livingston and with those for CO₂⁻ in order to decide with which directions they should be associated.

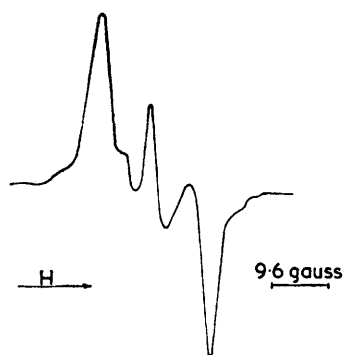


FIG. 1. Electron-spin resonance spectrum of γ -irradiated barium formate powder.



FIG. 2. Electron-spin resonance spectrum of NO₂ trapped in ice at 77°K. $a_1b_1 = b_1c_1 = a_{yy}$; $a_2b_2 = b_2c_2 = a_{xx}$; $a_3b_3 = b_3c_3 = a_{zz}$. g -Values measured at b_1, b_2, b_3 .

Solutions of nitrogen dioxide in carbon tetrachloride, chloroform, nitromethane, and dinitrogen tetroxide, at a range of temperatures and concentrations, give only a single, broad, spin-resonance absorption, having a g -value of about 2.000 and a width between points of maximum slope of about 150 gauss. Attempts to obtain rigid solutions of nitrogen dioxide by rapidly cooling in liquid nitrogen failed, presumably because dimerisation was complete.

Diffuse Reflectance Spectra.—Precautions were observed as outlined earlier,⁹ and results for irradiated formates and oxalates are summarised in Table 2. Bands at 340 and 280 μ are thought to be a property of CO_2^- radical-ions and were not found in the spectra of irradiated oxalates. This does not rule out the presence of CO_2^- in these crystals because the bands are of low intensity and the radical yield was also low. Unirradiated formates did not absorb in the near-ultraviolet region, but oxalates are characterised by an intense band at 255 μ .

DISCUSSION

The treatment for CO_2^- given by Ovenall and Whiffen³ seems to us to be most satisfactory and we fully accept their conclusions, summarised in Table 4. Our results do not differ sufficiently to warrant an alternative calculation. Our treatment for nitrogen dioxide follows exactly that³ for CO_2^- , except that in view of the considerable spin-density on oxygen we thought it advisable to consider what contribution this might make to the total anisotropic hyperfine splitting from ^{14}N .

Structure of Nitrogen Dioxide.—The resonance data for nitrogen dioxide may largely be interpreted in terms of the unpaired electron occupying a $4a_1$ molecular orbital constructed from nitrogen $2s$ and $2p_z$ and oxygen $2p_z$ atomic orbitals, having the form

$$\psi(4a_1) = a_s\psi_N(2s) + a_z\psi_N(2p_z) + b_1\psi_O(2p_z), \quad (\text{i})$$

and neglecting overlap. The z -axis is the C_{2v} symmetry axis of the molecule, the x -axis is perpendicular to the molecular plane, and the y -axis parallel to the oxygen-oxygen direction.

TABLE 4.
Parameters for CO_2^- and NO_2 .

XO_2	Source	Note	a_s^2	a_p^2	a_x^2	c	b_1^2	d	λ^2	OXO angle
NO_2	Zeldes <i>et al.</i> ⁶	a	0.094	0.386	0.054	0.52	0.33	0.33	4.04	132°
		b	0.103	0.471		0.43	0.33		4.50	134
,,	Present work	a	0.097	0.371	0.019	0.53			3.83	131
		b	0.106	0.452		0.45			4.26	134
,,	McEwen ¹⁵	e	0.098	0.263		0.63			2.68	
	Green <i>et al.</i> ¹⁴	e	0.168	0.222		0.61			1.32	
CO_2^-	Ovenall <i>et al.</i> ³		0.14	0.66	0.08	0.20	0.22		4.71	134

a Using $|\psi(0)|^2$ and $\langle r^{-3} \rangle$ data quoted by Holmberg, Livingston, and Smith, *J. Chem. Phys.*, 1960, **33**, 541. b Using data from Smith *et al.*¹¹ c Calc. by difference. d Calc. from Δg_y . e Theoretical.

a_s^2 , a_p^2 , a_x^2 , and b_1^2 give the unpaired electron density in the X $2s$, $2p_z$, $2p_x$ and oxygen $2p_z$ -orbitals. $\lambda^2 = a_p^2/a_s^2$.

The s -character of the $4a_1$ -orbital is obtained from the isotropic interaction term (A_{iso}) by using the expression

$$A_{\text{iso}} = g_N\beta_N(8\pi/3)|\psi_{2s}(O)|^2 \cdot a_s^2, \quad (\text{ii})$$

with $|\psi_{2s}(O)|^2 = 34.0 \times 10^{24} \text{ cm.}^{-3}$;¹⁰ Zeldes and Livingston's work⁶ gives $a_s^2 = 0.094$. If the results of Smith *et al.* are used,¹¹ $a_s^2 = 0.103$.

The dipolar interaction of an unpaired electron in the p_z -component of the $4a_1$ -orbital with the nitrogen nucleus can be expressed as a diagonal tensor (\mathbf{A}), axially symmetric about the z -axis and with zero trace. It has the form

$$\mathbf{A}_1 = \begin{pmatrix} -\alpha & & \\ & -\alpha & \\ & & 2\alpha \end{pmatrix}. \quad (\text{iii})$$

The experimental anisotropic hyperfine interaction tensor (\mathbf{A}) is not axially symmetric

⁹ Griffiths, Lott, and Symons, *Analyt. Chem.*, 1959, **31**, 1338.

¹⁰ Dousmanis, *Phys. Rev.*, 1955, **97**, 967.

¹¹ Smith, Sorokin, Gelles, and Lasher, *Phys. Rev.*, 1959, **115**, 1546.

but may be resolved into two axially symmetric tensors \mathbf{A}_1 and \mathbf{A}_2 , with the symmetry axis of \mathbf{A}_2 along the x -axis. Thus

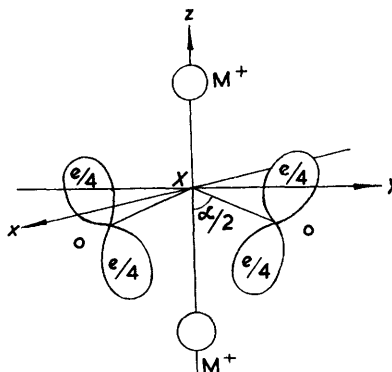
$$\mathbf{A} = \mathbf{A}_1 + \mathbf{A}_2 = \begin{pmatrix} -\alpha & & \\ & -\alpha & \\ & & 2\alpha \end{pmatrix} + \begin{pmatrix} 2\beta & & \\ & -\beta & \\ & & -\beta \end{pmatrix} \quad (\text{iv})$$

\mathbf{A}_2 probably arises³ from unpaired spin-density in the $2b_1$ -orbital which has $2p_x$ -character on nitrogen and is of the form

$$\psi(2b_1) = a_x \psi_N(2p_x) + b_2 \psi_O(2p_x), \quad (\text{v})$$

where the last term represents the contribution of the oxygen $2p_x$ -atomic orbitals. This explanation of \mathbf{A}_2 is preferred to that involving dipolar interaction from unpaired electron density on the oxygen atoms as this interaction is demonstrably small, and, although an

FIG. 3. Model used to calculate the dipolar interaction of a fraction of an electron in p -orbitals on oxygen of XO_2 . M^+ represent cations which interact with CO_2^- in $\text{H}\cdot\text{CO}_2\text{Na}$.



interaction tensor, axially symmetric about the x -axis, can be obtained, the signs of the elements are opposite to those of \mathbf{A}_2 . In this way, the results⁶ may be resolved into

$$\mathbf{A} = \begin{pmatrix} -5.27 & & \\ & -7.95 & \\ & & 13.22 \end{pmatrix} = \begin{pmatrix} -7.06 & & \\ & -7.06 & \\ & & 14.12 \end{pmatrix} + \begin{pmatrix} 1.78 & & \\ & -0.89 & \\ & & -0.89 \end{pmatrix} \text{ gauss} \quad (\text{vi})$$

The $2p_z$ -character of the $4a_1$ -orbital is obtained from

$$2\alpha = \frac{4}{5} g_N \beta_N \langle r^{-3} \rangle_{2p} \cdot a^2, \quad (\text{vii})$$

which is the explicit form of the dipolar interaction for the external field applied along the symmetry axis of the p_z -orbital. With $\langle r^{-3} \rangle_{2p} = 22.5 \times 10^{24} \text{ cm.}^{-3}$ when Dousmanis's values¹⁰ are used, $a_p^2 = 0.386$. When the values of Smith *et al.*¹¹ are used $a_p^2 = 0.471$. Similarly, on replacement of α by β , equation (vii) gives $a_x^2 = 0.049$. The total amount of electron accounted for is 0.48, leaving 0.52 to be shared between the two oxygen atoms.

The interaction of this fraction, e , with the nitrogen nucleus may be calculated approximately by assuming that one quarter of it ($e/4$ in Fig. 3) is in each lobe of the oxygen $2p_z$ -orbitals in such a way that the distance from the oxygen nuclei is the mean radius of these orbitals. \mathbf{A}_2 has been corrected for this contribution, the new value of a_x^2 being 0.054.

The ONO angle may be calculated by assuming that NO_2 is a trigonal planar molecule, and that the orthogonality relationships of Coulson¹² apply. For a hybridisation ratio $\lambda = a_p/a_s$, the bond angle (α) required is

$$\alpha = 2 \cos^{-1} (\lambda^2 + 2)^{-1/2}. \quad (\text{viii})$$

¹² Coulson, Victor Henri Volume Commemoratif, Contribution à l'Étude de la Structure Moléculaire, 1948, p. 15.

Introduction of the above values gives $\alpha = 132^\circ$ or 134° . These may be compared with the accepted value¹³ of 134° .

The low value for g_y accords with this treatment. In accord with Ovenall and Whiffen's treatment for CO_2^- , the departure (Δg_y) from the free-spin value is given by

$$\Delta g_y = -2(a_p a_x \zeta_N + 2b_1 b_2 \zeta_O)(a_p a_x + 2b_1 b_2) / \Delta E. \quad (\text{ix})$$

This may be rearranged to a quadratic in b_1 and the values of the parameters can then be inserted. Introducing the values obtained from Zeldes and Livingston's results,⁶ and using Green and Linnett's values for a_x and b_2 ,¹⁴ setting the one electron spin-orbit coupling parameters (ζ_N and ζ_O) equal to 70 and 152 cm^{-1} , respectively, and using $E = 13,200 \text{ cm}^{-1}$ for the vertical excitation energy for $B_1 \leftarrow A_1$, lead to $b_1 = 1.55$ or -0.57 . The former value is rejected as physically unacceptable and so we obtain $b_1^2 = 0.33$, in fair agreement with the earlier result (0.43).

Parameters calculated from both Zeldes and Livingston's and our own work are given in Table 4, together with those³ for CO_2^- . Also included are Green and Linnett's¹⁴ and McEwen's¹⁵ theoretical values.

Comparison of CO_2^- with NO_2^- .—The most striking feature of the results is the far greater localisation of the unpaired electron on carbon in CO_2^- than on nitrogen in NO_2^- . This is in accord with expectation, being a direct consequence of the greater nuclear charge on nitrogen. This effect draws paired electrons towards nitrogen more than towards carbon and this, in turn, results in a compensating tendency for the unpaired electron to avoid nitrogen more than carbon. Alternatively, one can picture the formation of these radicals by loss of an electron from the corresponding anions CO_3^{2-} and NO_3^- . Because of the greater electronegativity of nitrogen, the resulting "hole" will be centred relatively more on carbon than on nitrogen.

This result is also in accord with the chemical reactivity of the radicals. The greater delocalisation of the unpaired electron in nitrogen dioxide will oppose dimerisation more than is the case for CO_2^- , so that, despite charge repulsion, oxalate is stable, whereas dinitrogen tetroxide readily dissociates. Again a hydrogen atom adds to the carbon of CO_2^- preferentially, to give formate, whereas it adds to an oxygen atom of nitrogen dioxide to give nitrous acid.

Electronic Spectra.—Our results show that CO_2^- has a weak band at about 340 and a stronger band at 280 $\text{m}\mu$. A third band of slightly greater intensity found at 255 $\text{m}\mu$ may also be a property of this radical, but since oxalate has a band in exactly this region and some dimerisation is possible in heavily irradiated crystals, we are uncertain of this assignment. Since the first absorption band for nitrogen dioxide is in the visible region we were led to suggest² that both this and the 340 $\text{m}\mu$ band for CO_2^- must involve partial electron transfer from oxygen to carbon or nitrogen. However, there is good reason to believe that the lowest-lying transition for nitrogen dioxide is $2b_1 \leftarrow 4a_1$.¹⁵ The $2b_1$ level is π -antibonding, but like the $4a_1$ level, and for similar reasons, this is likely to be considerably more localised on carbon or nitrogen than on oxygen.

If this assignment is accepted, then there is no obvious reason why there should be a shift of over 10,000 cm^{-1} to higher energies on going to CO_2^- . Qualitatively, there are two factors which might account for the shift. One is a medium effect of a type which generally operates for ions in condensed phases and depends on the fact that the medium is disposed in such a way as to minimise the energy of the ground state of the ion and thus disfavors any excited state in which there is a considerable redistribution of charge. This can be of comparable energy to the much-discussed crystal field operating on transition-metal ions. One can particularise by suggesting that the movement of an electron out of the $4a_1$ -level is opposed by the cation located on the Z -axis and known to

¹³ Bird, *J. Chem. Phys.*, 1956, **25**, 1040.

¹⁴ Green and Linnett, *Trans. Faraday Soc.*, 1961, **57**, 1.

¹⁵ McEwen, *J. Chem. Phys.*, 1960, **32**, 1801.

be interacting considerably because of its contribution to the spin-resonance spectrum (Fig. 3). There are no neighbouring cations to stabilise the $2b_1$ -level in this manner. Such medium effects should be trivial for nitrogen dioxide. Another factor which is probably significant is that there is considerably greater overall atomic s -character in the $4a_1$ -level of CO_2^- than in that of nitrogen dioxide. Because of the depth of this orbital the overall energy will be lowered relative to the $2b_1$ -level which does not involve s -orbitals in a first approximation. These two factors might together account for the shift observed.

Rotation of Nitrogen Dioxide.—We are unable to account for the very large isotropic hyperfine coupling reported for solutions of nitrogen dioxide in carbon tetrachloride.⁴ All our attempts to resolve the single very broad line normally found for this oxide in a variety of solvents have failed. We think that the most probable reason for failure is that the rate of dimerisation and dissociation are sufficient to broaden the lines beyond the point of resolution. However, varying temperature, concentration, and solvent over a wide range never resulted in a resolved spectrum.

Presumably for this reason, several studies of nitrogen dioxide trapped in inert matrixes have been made.^{5,16} Jen *et al.*¹⁷ observed a spectrum characterised by three strong, asymmetric lines and three shoulders. They ignored the latter and identified the splitting between the main lines with the isotropic coupling for ^{14}N . The same interpretation has been made by Zeldes and Livingston.⁶ This leaves the shoulders unexplained and gives values for a_{iso} and g_{av} considerably different from the results presented above. A similar result was obtained by McDowell and his co-workers⁵ in certain cases, but they interpreted the extra features as arising from nitrogen dioxide trapped in a "lattice site" specifically different from the prevalent one. This view is based upon a similar interpretation of the spin-resonance spectra of hydrogen atoms trapped in various matrixes,¹⁷ and is further justified by similar results for trapped alkali-metal atoms.¹⁸ However, the properties of an uncharged triatomic molecule are far more dependent upon intra- than upon inter-molecular forces, in contrast to atoms, especially those studied.^{17,18}

We suggest that these complex spectra are better interpreted in the manner used above for nitrogen dioxide trapped in ice (Fig. 2). However, the spectra under consideration^{5,16} are simpler than that of Fig. 2, being in accord with expectation for an axially symmetrical molecule. This could arise if rotation about the y -axis is still rapid, but other modes are restricted. Then the relationships

$$\begin{aligned} 2g_{\perp} &= (g_x + g_z), & g_{\parallel} &= g_y, \\ 2A_{\perp} &= (A_x + A_z), & A_{\parallel} &= A_y \end{aligned}$$

should hold. This is in fact the case. That this mode of rotation should remain unrestricted in certain matrixes is reasonable, in view of the large bond angle of 134° , and the fact that nitrogen dioxide trapped in argon at 4°K is apparently rotating quite freely.⁵

Interaction with Cations.—That specific interaction with one cation should occur is unusual for systems of this type and is probably a consequence of the geometry of the trapping site rather than some specific affinity between the cation and CO_2^- . As has been stressed³ there are two sodium ions which could interact with the unpaired electron, both lying on the z -axis of the radical. Since the electron is in an orbital which has a considerable extension along this axis pointing away from the oxygens it seems probable that the cation nearest to carbon is the one that interacts significantly. The orbital on the alkali metal occupied by the unpaired electron has very slight p_z -character and relatively large s -character. The s -character increases on going from sodium to potassium,

¹⁶ Walsh, *J.*, 1953, 2266.

¹⁷ Jen, Foner, Cochran, and Bowers, *Phys. Rev.*, 1958, **112**, 1169.

¹⁸ Bowers, Cochran, Foner, and Jen, Fifth Internat. Symposium on Free Radicals, Uppsala, 1961, 26-1.

the values being approximately 2.6% for ^{23}Na and 8.5% for ^{39}K . The value for ^7Li is <2.8%. These results have been obtained by comparing the isotropic hyperfine coupling constants (Table 1) with the data for alkali-metal atoms in the gas phase. The interaction can be thought of as involving slight charge-transfer rather than specific bonding, probably similar to that observed for many radical-anions in poorly solvating liquids.¹⁹ It is noteworthy that this interaction increases as the electron affinity of the cation falls but that the cation orbital retains its predominantly *s*-character. To understand this observation we think that the environment must again be considered. Each cation is co-ordinated to oxygen of neighbouring formate ions. This co-ordination will oppose the charge-transfer, the effect falling on going from lithium to potassium. These two trends are in opposition, and the results imply that the co-ordination effect predominates in this instance.

The trends in *g*-values are consistent with this picture. As the tendency for charge-transfer falls, so the energy of the transition $4a_1 \leftarrow 1a_2$ should increase since the "electron-affinity" of the $4a_1$ -level is involved. Since the mixing of these levels contributes a positive increment to the *g_z*-value,³ this should result in a trend to higher *g_z*-values on going from lithium to potassium, in accord with experiment. This trend may be enhanced by a similar modification of the $1a_2$ -level, which is non-bonding on oxygen. Movement of an electron from this level will be opposed by co-ordination to neighbouring cations, the opposition decreasing on going down the Periodic Table.

We thank Messrs. J. A. Brivati and P. A. Trevalion for experimental assistance, the Department of Scientific and Industrial Research and Imperial Chemical Industries Limited for financial assistance, and The Esso Petroleum Company and the Department of Scientific and Industrial Research for grants (to N. K. and P. W. A.).

DEPARTMENT OF CHEMISTRY, THE UNIVERSITY, LEICESTER. [Received, January 19th, 1962.]

¹⁹ Adam and Wiessman, *J. Amer. Chem. Soc.*, 1958, **80**, 1518.
