Electron Spin Resonance Studies. Part XXXVI.[1] Formation of Ion-pairs by Semidiones and Related Radicals in Aqueous Solution

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The one-electron oxidation of some α-hydroxy-acids or the one-electron reduction of α-keto-acids or α-diketones, in aqueous solution, yields hydroxysemidiones or semidiones which, in the presence of an appropriate di- or tri-positive metal ion, give metal complexes; in some cases metal-ion splittings can be observed. Data relating to the structures of the complexes are reported and discussed.

THE e.s.r. spectroscopy of semidiones and their conjugate acids has been extensively investigated in non-aqueous media [2-4] but much less so in aqueous solution. Under the latter conditions, such radicals have been generated from biacetyl and other α-dicarbonyl compounds by reduction with α-hydroxy- or α-alkoxy-substituted carbon radicals,[5] or with the species $\cdot CO_2H$, $\cdot CO_2^-$, and $\cdot CMe_2\cdot NH_2$,[6] and the studies have furnished information about acid-base equilibria, *cis–trans* isomerism, and tautomerism.[5-7] More recently, the *in situ* radiolysis of basic aqueous solutions of α-hydroxy-acids has been shown to yield species of the type $\cdot CR(O^-)\cdot CO_2^-$.[8]

We now describe investigations of the effect of metal ions on the e.s.r. spectra of some semidiones and related species in aqueous solution. The radicals were generated either by the one-electron reduction of the corresponding dicarbonyl compound as described previously [6] or by oxidation of the corresponding acyloin or hydroxy-acid with the hydroxyl radical; [5] in some cases both methods were used. The results provide evidence for the formation of chelated radical anions in some systems and enable us to define the structural features necessary for their observation.

Radicals from α-Dicarbonyl Compounds.—The one-electron reduction of biacetyl at pH 6 with either $\cdot CH_2\cdot OH$ or $\cdot CO_2^-$ gave the isomeric semidiones (1) and (2) [5] in relative concentrations *ca.* 1 : 15 (*cf.* the ratio 1 : 19 for solution in dimethyl sulphoxide [9]). When a 0·1M-solution of magnesium sulphate was introduced through a third entry port of the mixing chamber, the ratio of the concentrations of these radicals dropped slightly, to *ca.* 1 : 22, and a third radical [a_H(6) 0·885 mT, *g* 2·0043] was observed the concentration of which was approximately one-tenth that of (2). The addition of other divalent metal ions (Zn^{2+}, Ca^{2+}, Ba^{2+}) in like manner had similar effects, the third radical having e.s.r. parameters dependent upon the metal ion and given in Table 1. By premixing the metal salt and biacetyl, the spectrum of the radical (1) could be completely quenched and approximately equal concentrations of its isomer (2) and the third radical could be observed.

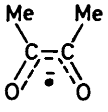
TABLE 1

Hyperfine splittings (mT) and *g*-factors for radicals from 1,2-dicarbonyl compounds RCO·COMe

R	Metal	a_H	*g*
Me [a]		0·715 (2Me)	2·0046
Me [b]		0·83 (2Me)	2·00455
Me	Mg^{2+}	0·885 (2Me)	2·0043
Me	Zn^{2+}	0·89 (2Me)	2·0040
Me	Ca^{2+}	0·87 (2Me)	2·00435
Me	Ba^{2+}	0·84 (2Me)	2·0041
H [a]		0·895 (Me), 0·62 (H)	2·0046
H [b]		0·96 (Me), 0·855 (H)	2·0043
H	Mg^{2+}	0·865 (Me), 1·005(H)	2·0038

[a] *trans.* [b] *cis.*

We infer that the extra radical observed on the addition of the metal ion is a chelate of the type (3) formed by the *cis*-semidione (1); interconversion between (1) and (3) is slow on the e.s.r. time scale (since their individual spectra were observed) but, under the conditions used, the formation of (3) is rapid enough, and (3) is stable enough, to increase the total concentration, (1) + (3), relative to that of the *trans*-semidione (2). It is notable that lithium, sodium, and potassium ions stabilise the *cis*- relative to the *trans*-form of the biacetyl semidione in dimethyl sulphoxide and splittings from ^7Li and ^{23}Na have been observed; [3,9] however, under our conditions the addition of a monopositive ion (lithium or sodium) had no observable effect.



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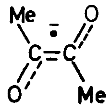

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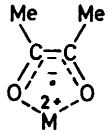

(3)

Likewise, the one-electron reduction of pyruvaldehyde at pH 6 gave the *cis*- and *trans*-semidiones [6] in about equal concentrations; when magnesium ions were

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[1] Part XXXV, B. C. Gilbert, J. P. Larkin, R. O. C. Norman, and P. M. Storey, *J.C.S. Perkin II*, 1972, 1508.

[2] G. A. Russell, P. R. Whittle, and R. G. Keske, *J. Amer. Chem. Soc.*, 1971, **93**, 1467, and references therein.

[3] G. A. Russell, J. L. Gerlock, and D. F. Lawson, *J. Amer. Chem. Soc.*, 1971, **93**, 4088.

[4] H. Zeldes and R. Livingston, *J. Chem. Phys.*, 1967, **47**, 1465; T. Fujisawa, B. M. Monroe, and G. S. Hammond, *J. Amer. Chem. Soc.*, 1970, **92**, 542; P. B. Ayscough and M. C. Brice, *J. Chem. Soc.* (*B*), 1971, 491.

[5] R. O. C. Norman and R. J. Pritchett, *J. Chem. Soc.* (*B*), 1967, 378.

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[7] R. J. Pritchett, *Mol. Phys.*, 1967, **12**, 481.

[8] G. P. Laroff and R. W. Fessenden, *J. Chem. Phys.*, 1971, **55**, 5000.

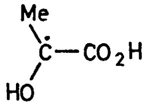
[9] G. A. Russell and R. D. Stephens, *J. Phys. Chem.*, 1966, **70**, 1320.

introduced in a third stream, the spectrum attributed[6] to the *trans*-semidione was unaffected, that attributed to its *cis*-isomer was reduced in intensity, and a third signal, ascribed to the metal chelate, appeared.

Radicals from α-Keto- or α-Hydroxy-acids.—The one-electron reduction of pyruvic acid at various pH values has been described.[6] The one-electron oxidation of lactic acid gave the same species, as well as others, but since under most conditions the resonances had much narrower line-widths when the radicals were generated from lactic acid, we examined this system in more detail.

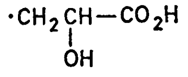
Oxidation of lactic acid at pH 1 gave the radical (4) [a_{H}(Me) 1·68, a_{H}(OH) 0·185 mT, *g* 2·0038], as from reduction of pyruvic acid at this pH,[6] together with (5) [$a_{\mathrm{H}}(CH_2)$ 2·215, a_{H}(CH) 2·665 mT, *g* 2·0027]; the relative concentrations of the two were *ca.* 10 : 1. The spectrum of the latter radical or its conjugate base was observed throughout the pH range studied, the conjugate base having a slightly different value for a_{H}(CH) (2·70 mT).

The radical (4) would be expected to occur in both *cis*- and *trans*-forms, and although only one was observed at pH 1, the spectrum of the other [a_{H}(Me) 1·66, a_{H}(OH) 0·18, $a_{\mathrm{H}}(CO_2H)$ 0·09 mT, *g* 2·0038] was apparent when



$\mathrm{Me(HO)\dot{C}{-}CO_2H}$

(4)



$\mathrm{\cdot CH_2CH(OH){-}CO_2H}$

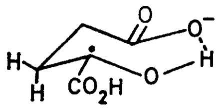
(5)

the pH was raised to 1·5; further increase in the pH caused the latter radical to increase in concentration relative to the former until, by pH 3, the ratio was at least 10 : 1. It is not possible unambiguously to assign the spectra to the *cis*- and *trans*-isomers; it may be that the isomer which is formed the faster is the one which predominates at pH 3 but that the other isomer is thermodynamically the more stable and predominates at pH 1 as the result of an acid-catalysed interconversion.

Above *ca.* pH 4, the lines in the spectrum began to broaden asymmetrically, probably as a result of exchange processes involving the *cis*- and *trans*-isomers of the radical (4) and its conjugate base, $\cdot CMe(OH)\cdot CO_2^-$ [the pK_a for (4) is[10] 5·3]. The lines sharpened at *ca.* pH 6 and then broadened on further increase in the pH, possibly as the result of exchange processes involving $\cdot CMe(OH)\cdot CO_2^-$ (pK_a 9·8[10]) and the radical dianion $\cdot CMe(O^-)\cdot CO_2^-$. However, at pH 13, with tartaric acid as sequestering agent (since the more commonly used EDTA gave spectra which partly obscured that from lactic acid and also caused precipitation), a spectrum with sharp lines [a_{H}(Me) 1·31 mT, *g* 2·0042] was again observed which is attributable to this radical dianion [*cf.* a_{H}(Me) 1·309 mT, *g* 2·00414 for this species generated by *in situ* radiolysis of a basic solution of lactic acid[8]].

Only at pH <*ca.* 2 or >*ca.* 10 were the lines in the spectrum obtained by oxidising glycollic acid sharp enough for unambiguous analysis; in between these pH limits, broadening probably results from exchange processes of the type we have discussed for radicals from lactic acid. At pH 1·3, the spectrum observed [a_{H}(1) 1·725, a_{H}(1) 0·255 mT, *g* 2·0038] is ascribed to the radical $\cdot CH(OH)\cdot CO_2H$, the larger and smaller doublet-splittings being attributed to CH and OH, respectively, although it is not known which geometrical isomer this is. At pH 10·7, the spectrum of the radical dianion $\cdot CH(O^-)\cdot CO_2^-$ was observed [a_{H}(CH) 1·43 mT, *g* 2·0043; *cf.* 1·424 mT, *g* 2·00435 for this species from *in situ* radiolysis of a basic solution of glycollic acid[8]].

The same general observations were made for the reduction of 2-oxobutyric acid; the radicals identified were $\cdot CEt(OH)\cdot CO_2H$ at pH 1·3 [$a_{\mathrm{H}}(CH_2)$ 1·09, a_{H}(OH) 0·19 mT, *g* 2·0038] and[8] $\cdot CEt(O^-)\cdot CO_2^-$ at pH 10—11. The behaviour of 2-oxoglutaric acid was slightly different. At pH 1, the radical $\cdot C(CH_2CH_2CO_2H)(OH)\cdot CO_2H$ was observed [$a_{\mathrm{H}}(CH_2)$ 1·24, a_{H}(OH) 0·18 mT]. As the pH was raised, an alternating line-width effect was observed; all the lines of the triplet broadened but the central line more than the other two and, by pH 4·5, the relative amplitudes of the triplet lines were 1 : 0·7 : 1, only the outside lines being narrow enough to show the small doublet splitting. This behaviour, which is in contrast to that shown by the radicals from lactic acid or the other oxo-acids, suggests that the β-methylene protons exchange environments at a rate somewhat less than the fast-exchange limit. A possible explanation is that the radical exists mainly in conformations of the type (6) and (7), dictated by internal hydrogen-bonding, interconverting between these conformations at a rate comparable with the hyperfine splitting interval between the differently sited β-protons; in accord with this, the line-width variation increases as the pH approaches the expected pK_a for the species (4—5). The line-width variations were no longer apparent at pH 6·5, all lines being equally broad, and the splitting from the hydroxy-proton was also absent at this pH.



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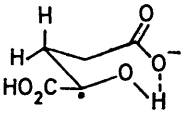

(7)

When an appropriate metal ion was introduced into the solutions for the oxidation of lactic or glycollic acid or the reduction of pyruvic, 2-oxobutyric, or 2-oxoglutaric acid, at a pH (6) greater than the pK_a of the corresponding carboxy-substituted radical, the broad-lined spectra were replaced by sharp-lined spectra attributable to metal chelates (Table 2). Two monovalent ions (lithium and sodium) were without effect,

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[10] M. Simic, P. Neta, and E. Hayon, *J. Phys. Chem.*, 1969, **73**, 4214.

and the introduction of either nickel(II) or copper(II) resulted in the disappearance of the spectra, presumably through one-electron oxidation of the radicals. Splitting from a metal nucleus with a magnetic moment was observed in the three cases of high natural abundance of such a nucleus (^{9}Be, 100%, *I* 3/2; ^{27}Al, 100%, 5/2; ^{139}La, 99·9%, 7/2); some extra, weak resonances in the spectra of complexes with aluminium suggested that other complexes might be present. In addition, the spectra from pyruvic acid or 2-oxobutyric acid with magnesium or zinc ions were intense enough to reveal satellite lines from ^{25}Mg (10%, *I* 5/2), ^{67}Zn (4%, 5/2), and ^{13}C (1%, 1/2). The ^{13}C-splittings are in Table 3; the values can be compared with those for the uncomplexed radical dianions $\cdot CMe(O^-)\cdot CO_2^-$ [1·409 (C_2), 0·819, 0·635 mT] and $\cdot CEt(O^-)\cdot CO_2^-$ [1·413 (C_2), 1·174 (C_4), 0·762, 0·624 mT],[8] and it is on this basis that we have assigned splittings to C_2 and, for the 2-oxobutyrate radicals, C_4. The assignments of the two smallest splittings in each case are tentative; it seems probable that methylation at C_3 in the lactate complex would affect $a(^{13}C_3)$ more than $a(^{13}C_1)$, so that the relatively constant splitting of *ca.* 0·65 mT is assigned to C_1 and the remaining splitting to C_3.

TABLE 2

Hyperfine splittings (mT) and *g*-factors for radicals from α-oxo-acids or α-hydroxy-acids

R	Metal	a_H	a_{metal}	g
Me	Be^{2+}	1·54 (3H)	0·03 (^{9}Be)	2·0039
Me	Mg^{2+}	1·39 (3H)	0·03 (^{25}Mg)	2·0040
Me	Ca^{2+}	1·35 (3H)		2·0041
Me	Ba^{2+}	1·33 (3H)		2·0039
Me	Zn^{2+}	1·40 (3H)	0·095 (^{67}Zn)	2·0038
Me	Al^{3+}	1·505 (3H)	0·15 (^{27}Al)	2·0039
Me	La^{3+}	1·37 (3H)	0·175 (^{139}La)	2·0032
H	Be^{2+}	1·60 (1H)	0·03 (^{9}Be)	2·0039
H	Mg^{2+}	1·49 (1H)		2·0042
H	Ca^{2+}	1·45 (1H)		2·0042
H	Ba^{2+}	1·425 (1H)		2·0041
H	Zn^{2+}	1·49 (1H)		2·0040
H	Al^{3+}	1·59 (1H)	0·16 (^{27}Al)	2·0041
Et	Mg^{2+}	0·92 (2H)	0·02 (^{25}Mg)	2·0040
Et	Ca^{2+}	0·875 (2H)		2·0040
Et	Zn^{2+}	0·94 (2H)	0·09 (^{67}Zn)	2·0038
Et	Al^{3+}	0·99 (2H)	0·16 (^{27}Al)	2·0039
Et	La^{3+}	0·86 (2H)	0·18 (^{139}La)	2·0032
$CH_2CH_2CO_2^-$	Mg^{2+}	1·17 (2H) 0·06 (2H)		2·0040
$CH_2CH_2CO_2^-$	Ca^{2+}	0·89 (2H) 0·05 (2H)		2·0040
$CH_2CH_2CO_2^-$	Ba^{2+}	0·925 (2H) 0·055 (2H)		2·0040
$CH_2CH_2CO_2^-$	Zn^{2+}	0·96 (2H) 0·05 (2H)		2·0038

TABLE 3

Hyperfine splittings (mT) from ^{13}C in metal complexes

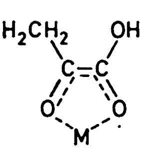
Organic unit: $\left[\overset{3}{C}H_3{-}\overset{2}{C}(O){-}\overset{1}{C}(O){-}OH\right]^{\bar{\cdot}}$

Metal ion	$a(^{13}C_1)$	$a(^{13}C_2)$	$a(^{13}C_3)$
Mg^{2+}	0·67	1·52	0·84
Zn^{2+}	0·655	1·525	0·82

Organic unit: $\left[\overset{4}{C}H_3{-}\overset{3}{C}H_2{-}\overset{2}{C}(O){-}\overset{1}{C}(O){-}OH\right]^{\bar{\cdot}}$

Metal ion	$a(^{13}C_1)$	$a(^{13}C_2)$	$a(^{13}C_3)$	$a(^{13}C_4)$
Mg^{2+}	0·64	1·51	0·785	1·20
Zn^{2+}	0·64	1·70	0·765	1·14

The complexes from 2-oxoglutaric acid showed a small triplet splitting (0·05—0·06 mT) which is assigned to the γ-methylene protons. It is notable that no such splitting was resolved in the spectrum of the uncomplexed radical, nor was there detectable splitting from the methyl-protons in the spectra of complexes from 2-oxobutyric acid [the line-widths (0·02, 0·03, and 0·025 mT, for the complexes with magnesium, calcium, and zinc, respectively) were such that a quartet splitting as small as 0·02 mT would have been discerned]. A possible explanation is that the extra carboxylate group in (8) is complexed to the metal ion so as either to bring the γ-protons into a favourable position for interaction with the spin or to allow delocalisation of the spin *via* this carboxylate group.



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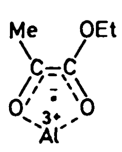

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The one-electron reduction of ethyl pyruvate gave the semidiones reported previously[6] and, in the presence of aluminium ions, a spectrum attributed to the chelate (9) with a_H(Me) 1·19, $a_H(CH_2)$ 0·05, $a(^{27}Al)$ 0·10 mT.

Finally, experiments in which magnesium ions were introduced into solutions generating the following radicals gave no evidence for the formation of metal complexes: $\cdot CH_2OH$, $\cdot CH_2O^-$, $\cdot CH_2CO_2^-$, $MeNO_2\cdot^-$, $\cdot CH(NH_3^+)\cdot CO_2^-$.

Structures of the Metal Complexes.—The structural requirements for the detection of metal ion–semidione complexes in aqueous solution, under the conditions we have employed, are as follows: the metal ion should be di- or tri-positive; the dione-forming species should have vicinal oxygen functions capable of achieving a *cis*-stereochemistry; the semidione should possess at least one negative charge [the α-keto-acids gave chelates only when the pH was greater than the pK_a of the species $\cdot CR(OH)\cdot CO_2H$], but the hydroxysemidiones may, at suitable pH, be present in the chelates as, formally, dianions.

The proton- and ^{13}C-splittings show small but significant variations as between the free and the complexed radicals and as between complexes with different metals. Values of A_0 (the calculated splitting for an unpaired electron in the outermost populated *s* orbital of an atom) are limited, but in the cases where they are available[11] it is apparent from the ratio of the observed metal splitting to A_0 that the *s*-orbital contribution from the metal ion is small; thus, the % *s*-orbital spin

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[11] P. W. Atkins and M. C. R. Symons, 'The Structure of Inorganic Radicals,' Elsevier, Amsterdam, 1967.

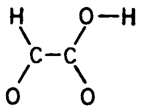
population in the complexes from lactic acid and glycollic acid is about 0·23 for beryllium (A_0 13·0 mT), 0·25 for zinc (A_0 37·6 mT), and 0·15 for aluminium (A_0 98·5 mT). The proton splittings seem likely to be determined, at least in part, by the size of the metal ion; as the data in Table 4 show, the proton-splittings, with some exceptions, decrease as the ionic radius of the metal increases. Finally, the *g*-factors are in every case lower for the metal complexes than for the free semidiones, consistent with there being some donation of spin from the semidione into an empty orbital of the metal ion;[11] in keeping with this, *g* is lowest for the heaviest atom (lanthanum).

TABLE 4

Ionic radii (Å) and proton hyperfine splittings (mT) for radicals from metal ions and hydroxysemidiones $[RC(O){\cdot}C(O){\cdot}OH]^{-\cdot}$

Metal ion	Ionic radius	R = H a_H	R = Me a_{Me}	R = Et a_{CH_2}
Be^{2+}	0·35	1·60	1·54	
Al^{3+}	0·50	1·59	1·505	0·99
Mg^{2+}	0·66	1·49	1·39	0·92
Zn^{2+}	0·74	1·49	1·40	0·94
Ca^{2+}	0·99	1·45	1·35	0·875
La^{3+}	1·06		1·37	0·86
Ba^{2+}	1·34	1·425	1·33	

We carried out an INDO calculation for the beryllium–glycollate complex. The organic fragment was considered both as (10) and its conjugate base, with bond angles of 120° and the following standard bond lengths:[12] C–H 1·08, C–O 1·36, C–C 1·40, O–H 0·96 Å. The beryllium ion was assumed to be equidistant from the two *cis*-oxygen atoms and was confined to the same plane as the atoms in the organic fragment. The Be–O distance was varied until the energy was minimised; this occurred at a separation of 1·61 Å, both with and without the hydroxy-proton, which is close to the value (1·64 Å) for crystalline beryllium oxide,[13] in accord with an essentially ionic interaction. The calculated *s*-orbital spin population for beryllium (after annihilation) was −0·003 or −0·001 (with or without the hydroxy-proton) (*cf.* the experimental value of |0·0023|), and the ionised form was found to have the higher calculated binding energy.



(10)

EXPERIMENTAL

A Varian E-3 spectrometer with an *X*-band klystron and 100 kHz modulation was employed. The attenuation was chosen to optimise the signal-to-noise ratio but to avoid saturation; a typical value was 15 mW, but in some cases the value was as low as 5 mW. The magnetic field was calibrated with an aqueous solution of Fremy's salt (a_N 1·3091 ± 0·0004 mT [14]) which also served as *g* marker (*g* 2·0055 [15]); splitting constants were measured to within ±0·005 mT and *g*-factors to within ±0·0001. The mixing chamber was either patterned on the Varian two-entry type or was a modification of this which allowed three reactants to be mixed simultaneously.

All materials were commercially available and were used without purification except for pyruvic acid, which was distilled *in vacuo* immediately before use. For the generation of radicals by the oxidation of a hydroxy-acid, one stream contained 100-volume hydrogen peroxide (3 g/l) and another contained 12·5% w/v titanium(III) chloride (10 ml/l), disodium ethylenediaminetetra-acetate (6 g/l) or tartaric acid [16] (for *ca.* pH > 2), and, where appropriate, the necessary amount of ammonia (*d* 0·880) to give the required pH; the hydroxy-acid (*ca.* 10 g/l) was contained in either one of these solutions or a third stream. For the generation of radicals by one-electron reduction, sodium formate (20 g/l) was included in the titanium(III) solution, the hydrogen peroxide concentration was reduced to 1—2 ml/l, and a solution of the carbonyl compound (1—3 g/l) formed a third stream. In some cases, notably reactions at high pH (9—11), improved signal-to-noise ratios were obtained by deaeration of the solutions with a nitrogen purge.

The concentration of metal salt was typically 0·1M, but complexes were formed with concentrations as low as 10^{-3}M; there were no detectable changes when the concentration was varied between 10^{-3} and 1M in specimen cases or when the anion was changed (*e.g.* $MgCl_2$ for $MgSO_4$). The metal salt was normally included in the solution containing the hydroxy-acid or carbonyl compound, but this was not essential (see discussion of the reduction of biacetyl).

We thank the S.R.C. for a studentship to A. J. D.

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[13] 'Tables of Interatomic Distances,' *Chem. Soc. Special Publ.* 11, 1958.

[14] R. J. Faber and G. K. Fraenkel, *J. Chem. Phys.*, 1967, **47**, 2462.

[15] J. Q. Adams, S. W. Nicksic, and J. R. Thomas, *J. Chem. Phys.*, 1966, **45**, 654.

[16] A. J. Dobbs, B. C. Gilbert, and R. O. C. Norman, *J.C.S. Perkin II*, 1972, 786.