

with six point charges at the corners of an octahedron and distorting the ligand-metal-ligand angle ( $b$ ) within the chelate plane.<sup>11</sup> Thus a geometrically right-handed molecule may have a trigonal potential (as well as all odd potentials) and rotational strength of either sign depending on the change of this angle,  $\Delta b$ , from  $90^\circ$ . For this reason it is not safe to conclude that two enantiomers with the same sign of  $R$  but with different ligands have the same configuration unless the ligands are very little different from one another.

From Table I it may be seen that the ionic model fails to account for the sign of  $K$  since there is no consistent correlation to  $\Delta b$ . Our studies of the acetylacetonate spectra indicate that the very anomalous intensities observed probably are due to the effects of  $\pi$ -covalency. These effects should be absent in the more ionic oxalates and indeed the signs of  $K$  and  $\Delta b$  for the chromium oxalate and ethylenediamine complexes do correlate. Thus we can say nothing for certain about the acetylacetonates, but we are led to the tentative conclusion that the trisoxalates which form the less soluble strychnine salts have the same absolute configuration as the (+)-D-Coen<sub>3</sub><sup>+3</sup> enantiomer.

NOTE ADDED IN PROOF.—Andrew D. Liehr has recently described (Sixth Int. Conf. Coord. Chem.) a covalent bond model which can account for the optical rotations. The sign depends primarily on an angle,  $\alpha$ , which the  $\sigma$ -bonding orbital makes with the metal-ligand bond axis. To apply this model, if we assume that the orbital is intermediate between  $sp^2$  and  $sp^3$ , then its angle to the O-C bond axis is  $115^\circ$ . Since the angles Cr-O-C are  $107^\circ$  and  $131^\circ$  in the oxalate and acetylacetonate, respectively, this model apparently makes the same incorrect prediction as the ionic model, namely, that in these compounds K (as well as R) should have opposite signs. However the model also contains  $\pi$ -bonding and overlap parameters which will have to be included in a complete calculation since they may affect the sign.

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(11) H. Hartmann, C. Furlani and A. Buerger, *Z. physik. Chem. (Frankfurt)*, **9**, 62 (1956).

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## ELECTROLYTIC GENERATION OF RADICAL IONS IN AQUEOUS SOLUTION

Sir:

The electrolytic generation of radical ions directly in the microwave cavity of an EPR spectrometer was introduced in 1959 by Maki and Geske.<sup>1</sup> A great deal of interest has developed in this technique and already a considerable body of information has been obtained on both anion and cation radicals.<sup>2-4</sup>

Such generations have not been attempted in aqueous solution, probably because the prevailing theories of voltammetry imply that especially nega-

- (1) A. H. Maki and D. H. Geske, *J. Chem. Phys.*, **30**, 1356 (1959).
- (2) D. H. Geske and A. H. Maki, *J. Am. Chem. Soc.*, **82**, 2671 (1960).
- (3) A. H. Maki and D. H. Geske, *J. Chem. Phys.*, **33**, 825 (1960); *J. Am. Chem. Soc.*, **83**, 1852 (1961).
- (4) M. T. Melchior and D. H. Geske, *ibid.*, **34**, 471 (1961).

tive ion radicals cannot be generated in proton rich solvents since a rapid, irreversible protonation followed by further electrochemical reduction occurs.<sup>5,6</sup> We wish to report the successful generation of both cation and anion radicals and especially negative ions from *aliphatic* nitro compounds in ordinary aqueous solutions.

The electrolysis vessel consisted of a rectangular aqueous cell inserted in the cavity of a standard Varian V-4500 EPR spectrometer using 100 Kc. field modulation. The supporting electrolyte was 0.1 *M* lithium perchlorate or 0.5 *M* potassium chloride or acetate buffer. In some cases 10-30% 1-propanol was added to improve solubility.

The mono-negative ions of *o*-, *m*- and *p*-nitroaniline; *o*-, *m*- and *p*-nitrophenol, *p*-nitroanisole, *p*-nitrodiphenylamine and nitrobenzene itself were generated and detected at a mercury pool electrode. The e.p.r. spectra were all well resolved and the hyperfine structure interpreted in terms of the molecular structure. The e.p.r. spectra of the *para* and *meta* isomers of nitroaniline, *p*-nitroanisole and nitrobenzene have been reported in acetonitrile very recently.<sup>3</sup> In water the N<sup>14</sup> coupling constants are some 3-4 gauss larger than in acetonitrile. It was observed that the radical ions decayed by a first order reaction (with a half-life of *ca.* 2 sec.) when the current was turned off. Such a decay strongly suggests reaction with the solvent and not with another ion.

The spectra of the mono negative ions of aliphatic nitro compounds show a very strong N<sup>14</sup> coupling and, in addition, coupling of the unpaired electron with protons on the carbon adjacent to the nitrogen. The N<sup>14</sup> coupling constants are summarized in Table 1. Figure 1 shows a typical spectrum. It is very interesting that these aliphatic anions exhibit such

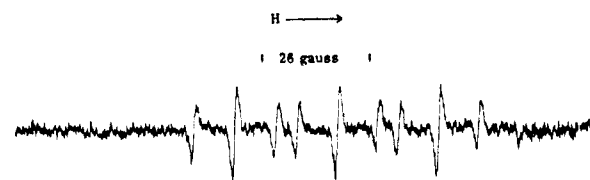


Fig. 1.—E.p.r. spectrum of 1-nitropropane negative ion in aqueous solution.

stability, especially in aqueous media. Only in the case of nitromethane was it not possible to obtain a spectrum with satisfactory signal/noise, although evidence of the radical ion was obtained. The widespread feeling that radical anions are too unstable *per se* to be observed by electrogeneration in aqueous media is rendered untenable by the present studies.

The stability of radical cations in aqueous solution has been known for years but electrogenerations of such species again have only been reported in acetonitrile.<sup>4</sup> Satisfactory generation and detection of the positive ions of *p*-phenylenediamine, N,N-dimethyl-*p*-phenylenediamine (Wurster's red), *o*-tolidine, N,N'-tetramethylbenzidine, *p*-amino-

- (5) G. J. Hoijtink, J. van Schooten, E. de Boer and W. Y. Aalbersberg, *Rec. trav. chim.*, **73**, 355 (1954).
- (6) P. H. Geiger and M. E. Peover, *Advances in Polarography (Proc. 2nd Int'l. Polarog. Cong., Cambridge)*, Vol. 3, p. 948 (1959).

TABLE I  
N<sup>14</sup> COUPLING CONSTANTS

Negative ion radical <sup>a</sup>	a <sub>N</sub>  , gauss
Nitroethane	25.2
1-Nitropropane	24.8
2-Nitropropane	25.4
1-Nitrobutane	24.3
2-Nitrobutane	24.5

<sup>a</sup> All generated in background electrolyte of 0.4 M KCl with 10% 1-propanol for solubility.

diphenylamine and several derivatives of chloro-promazine has been carried out in aqueous buffers.

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#### ON THE MECHANISM FOR LONG RANGE PROTON SPIN COUPLINGS

Sir:

In a recent paper, Kreevoy, *et al.*,<sup>1</sup> question the evidence for hyperconjugation as a mechanism for long range coupling in unsaturated compounds<sup>2</sup> such as propargyl derivatives and suggest that  $\alpha$ -hydrogen bonding<sup>3</sup> should be involved instead. They refer to recent theoretical work by Karplus<sup>4</sup> which, they claim, utilized essentially the  $\alpha$ -hydrogen bonding model. This latter assertion is not valid. Though Karplus states explicitly<sup>4</sup> that "the orbitals on the protons H and H' whose coupling is being determined are taken to be part of the sigma-electron system, this does not imply that hyperconjugation is not involved in his theory, since the proton spin coupling, as calculated by Karplus, is expressed in terms of hyperfine coupling constants and triplet state energies. Now the hyperfine coupling constants are obtained from e.s.r. data on related free radicals and insofar as the fragments

$\text{H}-\overset{\cdot}{\text{C}}-\overset{\cdot}{\text{C}}$  are concerned all theoretical interpretations<sup>5,6</sup> involve hyperconjugation either in its molecular orbital<sup>5</sup> or valence bond<sup>6</sup> formulation.

Thus the successful theoretical treatment of long range coupling<sup>4</sup> depends ultimately on hyperconjugation, rather than on the use of the  $\alpha$ -hydrogen bonding model.

(1) M. M. Kreevoy, H. B. Charman and D. R. Vinard, *J. Am. Chem. Soc.*, **83**, 1978 (1961).

(2) (a) R. A. Hoffman, *Mol. Phys.*, **1**, 326 (1958); (b) E. B. Whipple, J. H. Goldstein and L. Mandell, *J. Chem. Phys.*, **30**, 1109 (1959); (c) E. B. Whipple, J. H. Goldstein and W. E. Stewart, *J. Am. Chem. Soc.*, **81**, 4761 (1959); (d) A. D. Cohen and N. Sheppard, *Proc. Roy. Soc. (London)*, **A252**, 488 (1959); (e) P. L. Corlo and I. Weinberg, *J. Chem. Phys.*, **31**, 569 (1959); (f) R. A. Hoffman and S. Gronowitz, *Acta Chem. Scand.*, **13**, 1477 (1959).

(3) M. M. Kreevoy and H. Eyring, *J. Am. Chem. Soc.*, **79**, 5121 (1957).

(4) M. Karplus, *J. Chem. Phys.*, **33**, 1842 (1960).

(5) (a) R. Bersohn, *ibid.*, **24**, 1066 (1956); (b) D. B. Chesnut, *ibid.*, **29**, 43 (1958).

(6) (a) A. D. McLachlan, *Mol. Phys.*, **1**, 233 (1958); (b) P. G. Lykos, *J. Chem. Phys.*, **32**, 625 (1960).

Apparently<sup>7</sup> the fundamental difference between hyperconjugation and  $\alpha$ -hydrogen bonding is that whereas hyperconjugation depends upon a non-vanishing magnitude for the exchange integral between a carbon  $p\pi$ -orbital and the tetrahedral hybrid on an  $\alpha$ -carbon,  $\alpha$ -hydrogen bonding requires a non-vanishing magnitude for the exchange integral between the  $p\pi$ -orbital and an  $\alpha$ -hydrogen  $1s$ -orbital.

Until calculations have demonstrated that acceptable estimates of the latter integral can account for the magnitudes and signs of observed long range couplings, it seems more reasonable to interpret these couplings in terms of hyperconjugation. More elaborate arguments and evidence in support of this view may be found in some recent works.<sup>8</sup>

(7) M. M. Kreevoy, *Tetrahedron*, **5**, 233 (1959).

(8) (a) R. A. Hoffman and S. Gronowitz, *Arkiv Kemi*, **16**, 471 (1960); (b) R. A. Hoffman, *ibid.*, **17**, 1 (1960).

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#### ON d HYBRIDIZATION IN CHLORINE

Sir:

The use of hybridization in valence bond theory in order to explain observed molecular geometries is well known. The classic example is of  $sp^3$  hybridization in the group IV elements. In this case the bonding configuration (valence state) is considerably above the ground state in energy. The necessary promotion energy is regained upon bond formation yielding, of course, a stable molecule.

It is known that compounds of fluorine and chlorine exhibit many differences in structural properties. These differences frequently have been attributed to d hybridization in chlorine. Since chlorine has valence electrons in the 3s and 3p shells, excitation of these electrons to the 3d orbital has been assumed to be relatively easy in contradistinction to fluorine where the necessary excitation is 2s and 2p to 3d. The argument of easy orbital excitation when the principal quantum number remains unchanged is based in essence upon the assumption that the field in which the valence electrons move is reasonably close to coulombic.

In fluorine the energy of the center of gravity of states arising from  $2s^2 2p^4 (^3P) 3d$  is 15.9 e.v.<sup>1</sup> Until recently the energy location of states arising from the configuration  $3s^2 3p^4 3d$  in chlorine was unknown. Humphreys and Paul<sup>2</sup> and Minnhagen<sup>3</sup> have analyzed the chlorine spectrum. From their assignments the center of gravity of states arising from  $3s^2 3p^4 (^3P) 3d$  is 11.2 e.v.

In both fluorine and chlorine the excitation energy is large, in each instance being slightly less than 2 e.v. below the ionization limit. It would thus appear arbitrary to select the configuration of chlorine involving 3d electrons from the wealth of configurations near the ionization limit. In view of

(1) Charlotte E. Moore, "Atomic Energy Levels," Vol. I, United States Department of Commerce, 1949, Washington, D. C.

(2) C. J. Humphreys and E. Paul, Jr., *J. Opt. Soc. Am.*, **49**, 1186 (1959).

(3) L. Minnhagen, *ibid.*, **51**, 298 (1961).