oxide by mass-spectrometer spectral patterns and by comparison of the infrared spectra with the spectra of the *cis* and *trans* forms of 2,3-epoxybutane. The mass spectra, with parent masses at 112 to 117 mass units, give the empirical formula $C_2H_2Cl_2O$ from isotope ratio arguments. Chemical analysis for C, H, and Cl yielded 21.2%, 1.97%, and 63.5% for oxide I; and 21.2%, 1.92%, and 63.6% for oxide II. The calculated values for $C_2H_2Cl_2O$ are 21.27%, 1.78%, and 62.78%.

Known compounds of this composition, dichloroacetaldehyde and chloroacetyl chloride, were shown to differ from oxide I and oxide II in both mass spectrometer ionization patterns and GLP chromatographic retention times.

The properties, b.p., m.p., $d^{25}{}_4$ and $n^{24}{}_D$ found for these compounds are oxide I: 80–81°, −43°, 1.405 and 1.438; oxide II, 111–112°, −63°, 1.470 and 1.452. From present information it has not been possible to decide unequivocally which compound is the *cis*-isomer and which is the *trans*-isomer.

At present one can only speculate as to the origin of these compounds. Yields of oxide I as high as $G = 9$ were found in old samples of irradiated *trans* 1.2-dichloroethylene. As this is as large as the total yield of "polymer" determined immediately after irradiation, a chain reaction for the formation of the oxides is indicated. An attractive possibility is an auto-oxidation reaction using a long-lived free radical present in very low concentration as the intermediate. Preliminary tests with other sources of radicals (benzoyl peroxide) in the presence of oxygen showed that small yields of both the dichlororethylene oxides are formed from both *cis*- and *trans*-1,2-dichloroethylenes.

This work was performed under the auspices of the United States Atomic Energy Commission.

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RECEIVED JUNE 30, 1958

SIMPLE METAL ORBITAL TREATMENT OF THE BINDING OF THE HYDROGEN ATOM IN COBALT CARBONYL HYDRIDE

Sir:

On the basis of nuclear resonance and acid dissociation constants, Cotton and Wilkinson[1] have suggested that protons in $HCo(CO)_4$ and $H_2Fe(CO)_4$ are physically close to and primarily bound to the metal atoms. Liehr[2] has discussed which metal orbitals might be used in bonding. Edgell and Gallup[3,4] consider the proton in $HCo(CO)_4$ to be placed so far from the Co atom (~2.0 Å.) that it is primarily bound to the carbon pπ orbitals. This view seems to be based on observed splitting of CO stretching frequencies while corresponding Co–C modes appear unsplit by the proton (according to their assignments). Since such reasoning seems in principle valid, we note that Stammreich[5] has recently observed distinct splittings of *all* triply degenerate vibrations in going from $Fe(CO)_4^{-2}$ to $HFe(CO)_4^-$.

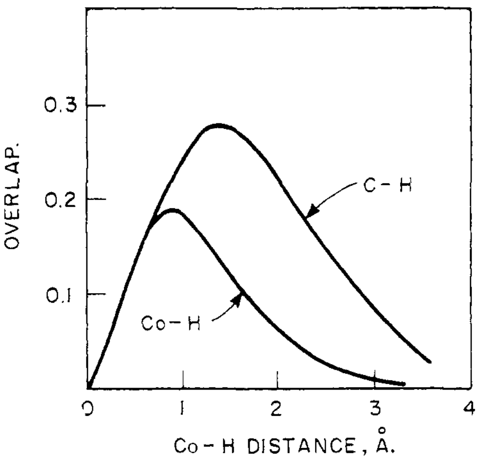

Fig. 1.

In an effort to substantiate their view, Edgell and Gallup[4] reported that a calculation of overlaps shows "that the hydrogen overlap integrals all have a maximum at a Co–H distance just short of 2 Å. . . ."[6] and they call attention to "the relatively large value of the $\phi_H\phi_C$ overlap and the relatively small value of the $\phi_H\phi_{Co}$ overlap." We question whether this type of calculation is as meaningful as they suggest, but granting that it is, there appear to be large numerical errors in their results. Repeating this calculation [(1) placing the hydrogen atom on a C_3 axis of the $Co(CO)_4$ tetrahedron and computing overlaps over the d_{Co-H} range 0.2 to 3.0 Å.; (2) taking S(Co-H) as $S(1s - 3d_{z^2})$; (3) computing for S(C–H) the overlap of the H 1s orbital with a simple LCAO-MO of A_1 symmetry, *viz.*, $1/\sqrt{3}[p\pi_{C_1} + p\pi_{C_2} + p\pi_{C_3}]$; (4) deriving the master formula for $S(1s - 3d_{z^2})$ and using published tables of integrals for Slater orbitals[7]] the results shown in the figure were obtained.

Features of principal interest are: (1) Both the Co–H and C–H overlaps are of comparable magnitude. (2) The C–H overlap maximizes at ~1.4 Å. while the Co–H overlap maximizes at ~0.9 Å. (3) The greatest total overlap (~40% Co–H and ~60% C–H) occurs at $d_{Co-H} \simeq 1.2$ Å. The relative magnitudes of S(Co–H) and S(C–H) could be further altered in favor of S(Co–H) by including overlap in calculating the normalizing factor for the carbon pπ MO and by calculating S(Co–H) using for Co a $3d_{z^2}$–$4p_3$ hybrid orbital. However, taking the results as they are, they suggest that Co–H bonding is quite important and that the hydrogen atom lies within 1.2 Å. of the Co atom. Since the sum of the Co and H radii is 1.2–1.4 Å., it appears not unjustified to describe the proton as somewhat

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[1] F. A. Cotton and G. Wilkinson, *Chemistry and Industry* (*London*), 1305 (1956).

[2] A. D. Liehr, *Z. Naturforsch.*, **12b**, 95 (1957).

[3] W. F. Edgell, C. Magee and G. Gallup, THIS JOURNAL, **78**, 4185 (1956).

[4] W. F. Edgell and G. Gallup, *ibid.*, **78**, 4188 (1956).

[5] H. Stammreich, private communication, to be published shortly.

[6] Note that when $d_{Co\text{-}H} = 2.0$ Å., $d_{C\text{-}H} = \sim 2.2$ Å., *i.e.*, about twice the normal C–H bond distance; yet a total C–H overlap of ~0.64 was reported.[4] It was the improbability of this result which led to the present recalculation.

[7] (a) M. Kotani, A. Amemiya, E. Ishiguro and T. Kimura, *Tables of Molecular Integrals*, Maruzen Co., Tokyo, Japan (1955); (b) R. S. Mulliken, C. A. Rieke, D. Orloff and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).

buried in the electron density of the cobalt atom as has been suggested[1] previously whereas these numerically accurate calculations provide no support for a Co-H distance of $\sim$2.0.

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RECEIVED JULY 7, 1958

FORMATION OF GUANOSINE DIPHOSPHATE FUCOSE FROM GUANOSINE DIPHOSPHATE MANNOSE

Sir:

A fucose containing nucleotide, guanosine diphosphate fucose, has been isolated recently from sheep milk[1] and from *Aerobacter aerogenes*.[2] It has now been found that GDPM[3] can be converted to guanosine diphosphate fucose by dialysed crude extracts of *A. aerogenes*[4] in the presence of TPNH.

The conversion was detected as follows: GDPM, prepared from yeast,[5] was incubated with TPNH and crude bacterial extracts obtained by shaking the cells with glass beads[6] followed by centrifugation and dialysis. The guanosine sugar nucleotides were then isolated and purified from the incubation mixtures by charcoal adsorption and paper chromatography.[5] Chromatography of the sugar liberated by 0.01 N HCl hydrolysis of the isolated nucleotides revealed, in addition to mannose, the presence of a second compound. This new compound exhibited the characteristic 400 mμ absorption peak when examined by the specific colorimetric assay for 6-deoxyhexose.[7] Upon paper chromatography, the unknown sugar co-chromatographed with authentic fucose using the solvents 2-butanone–acetic acid–saturated boric acid solution,[8] butanol–acetic acid–water,[9] phenol–water[9] or pyridine–ethyl acetate–water.[10] These solvents readily distinguish fucose from rhamnose. Further evidence for the identity of this sugar was indicated by the fact that it was active as a substrate for L-fucose isomerase.[11] The reaction product, presumably L-fuculose, was detected by means of the cysteine–carbazole reaction.[11,12]

TABLE I

CONVERSION OF GUANOSINE DIPHOSPHATE MANNOSE TO GUANOSINE DIPHOSPHATE FUCOSE

The reaction mixtures contained 1.0 μmole GDPM, 4 mg. of crude extract protein and additions in 1.0 ml. of 0.05 M tris-(hydroxymethyl)-aminomethane buffer, pH 7.8. Incubation was carried out at 37° for 4 hours. The nucleotides were then adsorbed on charcoal and the nucleotide bound sugars liberated by heating for ten minutes at 100° in 0.01 N HCl. After deionization with Amberlite MB-3, the fucose in the hydrolysate was estimated colorimetrically[7] or by paper chromatography.

Additions	μmole fucose formed
None	<0.02
2.0 μmoles TPN	0.05
2.0 μmoles TPNH	0.40
2.0 μmoles DPNH	<0.02
2.0 μmoles TPNH and 1.0 μmole GTP in place of GDPM	<0.02

The requirement for TPNH is shown in Table I. It is evident from structural considerations that the formation of the L-fucose derivative is a complex reaction which probably involves several steps. The nature of these steps remains to be elucidated.

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[1] R. Denamur, G. Fauconneau and G. Guntz, *Compt. rend.*, **246**, 2820 (1958).

[2] V. Ginsburg and H. N. Kirkman, THIS JOURNAL **80**, 3481 (1958).

[3] Abbreviations: GDPM, guanosine diphosphate mannose; GTP, guanosine triphosphate; TPNH, reduced triphosphopyridine nucleotide; TPN, triphosphopyridine nucleotide; DPNH, reduced diphosphopyridine nucleotide.

[4] Strain A_3S_1 (ATCC 12657).

[5] E. Cabib and L. F. Leloir, *J. Biol. Chem.*, **206**, 779 (1954).

[6] P. M. Nossal, *Australian J. Exptl. Biol.*, **31**, 583 (1953).

[7] Z. Dische and L. B. Shettles, *J. Biol. Chem.*, **175**, 595 (1948).

[8] W. R. Reis and T. Reynolds, *Nature*, **181**, 768 (1958).

[9] S. M. Partridge, *Biochem. J.*, **42**, 238 (1948).

[10] M. A. Jermyn and F. A. Isherwood, *ibid.*, **44**, 402 (1949).

[11] M. Green and S. S. Cohen, *J. Biol. Chem.*, **219**, 557 (1956).

[12] Z. Dische and E. Borenfreund, *ibid.*, **192**, 583 (1951).

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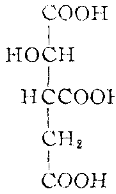
RECEIVED JULY 7, 1958

CRYSTALLOGRAPHIC EVIDENCE FOR THE RELATIVE CONFIGURATION OF NATURALLY OCCURRING ISOCITRIC ACID[1]

Recently Greenstein and his co-workers[2] have studied the stereochemistry of the isocitric acids and alloisocitric acids and have concluded that the configuration of the α-carbon atom in the naturally occurring isocitric acid is L$_S$. Gawron and Glaid,[3] on the basis of pK measurements, have concluded that in the isocitric acid lactone the two carboxyl groups are *cis* with respect to the γ-lactone ring while in that of alloisocitric acid the two carboxyls are *trans*. Thus, if the α carbon is in the L configuration, the formula in the Fischer convention for the naturally occurring isocitric acid is I.



$$\begin{array}{l} COOH \\ | \\ HOCH \\ | \\ HCCOOH \\ | \\ CH_2 \\ | \\ COOH \end{array}$$

I

Through the kindness of Dr. H. B. Vickery and Dr. D. G. Wilson of the Connecticut Agricultural Experiment Station we have been able to carry out an X-ray structure analysis on excellent crystals of the monopotassium and monorubidium salts of the lactone prepared by them from the isocitric acid occurring in the leaves of *Bryophyllum calycinum*. These salts are isomorphous on the orthorhombic

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[1] Supported by a grant (C1253) from the National Cancer Institute, Public Health Service.

[2] (a) J. P. Greenstein, N. Izumiya, M. Winitz and S. M. Birnbaum, THIS JOURNAL, **77**, 707 (1955); (b) M. Winitz, S. M. Birnbaum and J. P. Greenstein, *ibid.*, **77**, 716 (1955).

[3] O. Gawron and A. J. Glaid III, *ibid.*, **77**, 6638 (1955).