Table I. Electrochemical Reduction of Carbonyl Compounds in Strongly Acidic Medium

Starting material	Product	Mp, °C	Yield, %	Electrolysis time, hr
17β-Hydroxy-5α-androstan-3-one	5α-Androstan-17β-ol	162–164	97	3.5
3-Methoxy-1,3,5(10)-estratrien-17-one	3-Methoxy-1,3,5(10)-estratriene	77.5–78.5	94	20
17α,20:20,21-Bismethylenedioxy-3β-acetoxypregn-5-en-19-one	17α,20:20,21-Bismethylenedioxy-3β-hydroxypregn-5-ene[a]	242–245	90	4
3β-Hydroxypregn-5-en-20-one	3β-Hydroxypregn-5-ene	133–134	96	5.5
3β,17α-Dihydroxypregn-5-en-20-one	3β-Hydroxypregn-5-ene	133–134	85	6

[a] The product was hydrolyzed by heating it with sodium hydroxide in methanol to yield the free alcohol.

Table II. Deuterium Incorporation by Electrochemical Reduction of Carbonyl Compounds

Starting material	Product	Mp, °C	Isotope composition,[a] % d_0	d_1	d_2	d_3	d_4	d_5
Estrone	Estra-1,3,5(10)-trien-3-ol-17,17-d_2	133–135		6	89	5		
Estrone-16,16-d_2 methyl ether[b]	3-Methoxy-1,3,5(10)-estratriene-16,16-d_2	76–78		6	94			
3β-Hydroxypregn-5-en-20-one	Pregn-5-en-3β-ol-20,20-d_2	134–136		4	84	11	1	
17β-Hydroxy-5α-androstan-3-one	5α-Androstan-17β-ol-3,3-d_2 acetate[c]	80–81.5		1	33	34	25	7
17α,20:20,21-Bismethylenedioxy-3β-acetoxypregn-5-en-19-one	17α,20:20,21-Bismethylenedioxy-3β-acetoxypregn-5-ene-19,19-d_2	170–172	1	6	93			
5α-Cholest-22-en-16-one[d]	5α-Cholest-22-ene-16,16-d_2	96.5–97.5		7	90	3		

[a] The isotope composition was determined mass spectrometrically. [b] The deuterium exchange was carried out by heating under reflux for 48 hr a solution of estrone methyl ether in 90% tetrahydrofuran and 10% deuterium oxide containing a drop of 10% sodium deuterioxide in deuterium oxide. Isotope composition: 5% d_1 and 95% d_2. The reduction was carried out in a protic medium. [c] The reduction product was acetylated with acetic anhydride in pyridine to facilitate purification. [d] This reaction was carried out by Dr. S. G. Wyllie at the Chemistry Department, Stanford University.

ment of the cell.[4] The same electrolyte was used in the anode compartment. The cell was kept at room temperature, the cathode compartment was magnetically stirred, and the current was kept constant at 200 ma. The progress of the reduction was followed by spot testing the reaction mixture directly on thin layer chromatographic plates.

The reduction of some typical steroidal ketones to their methylene analogs proceeded in high yield (see Table I). The thermodynamically more stable alcohol epimer[2] is usually observed as a minor side product (*ca.* 5%). These alcohols resisted further reduction under the same reaction conditions and, therefore, are not reaction intermediates. The observed reductive cleavage of the hydroxyl function α to the carbonyl group in 3β,17α-dihydroxypregn-5-en-20-one (see Table I) is in agreement with the observations of Kabasakalian, *et al.*[2] Other hydroxyl groups are unaffected.

Incorporation of two deuterium atoms in place of the carbonyl group can be achieved with a high degree of isotopic purity (see Table II). This method[5] provides an easy means of labeling certain positions on the steroid nucleus, such as the C-17,[6,7] C-19,[8] and C-20[6] positions, which have proven difficult to attain by the application of the usual chemical reaction sequences. Deuterium exchange of the enolizable protons α to the carbonyl groups appears to be the major cause of isotopic impurity and it is more pronounced for ketones such as at C-3, for example, for which the enolization is extremely rapid. This technique can also be employed to introduce deuterium atoms onto the carbon atoms adjacent to the carbonyl group by exchanging the enolizable protons with deuterium atoms, followed by the cathodic reduction of the carbonyl group in a protic medium (see the entry for estrone-16,16-d_2 methyl ether in Table II).

Examination of the scope of this reaction and its extention to α,β-unsaturated ketones and other functionalities is currently in progress.

Lewis Throop, Lászlo Tökés
Institute of Steroid Chemistry, Syntex Research
Palo Alto, California 94304

Received June 12, 1967

---

[4] The electrolyses were performed in a divided cell equipped with a cellulose dialysis membrane. The electrodes were cut from a 1.5-mm-thick lead sheet.

[5] The deuterium-labeled hydrocarbons were prepared in a microcell by using 6 ml of reagent grade dioxane and 6 ml of 10% deuteriosulfuric acid in deuterium oxide (deuterium content 97%) in both compartments. In order to prevent isotope dilution by atmospheric moisture, the air spaces in the cells were flushed with a slow current of dry nitrogen.

[6] C. Djerassi and L. Tökés, *J. Am. Chem. Soc.*, 88, 536 (1966).

[7] An improved method for the preparation of androstane-17,17-d_2 *via* the lithium aluminum deuteride reduction of the *p*-toluenesulfonylhydrazone of the 17-ketone was reported by L. Tökés, Ph.D. Dissertation, Stanford University, 1965.

[8] C. Djerassi and M. A. Kielczewski, *Steroids*, 2, 125 (1963); R. H. Shapiro, D. H. Williams, H. Budzikiewicz, and C. Djerassi, *J. Am. Chem. Soc.*, 86, 2837 (1964).

The Radiation Cross-Linking of Hydrogenated Polyethylene[1]

Sir:

Cross-linking of linear polyethylene induced by high-energy irradiation has been shown to be dependent on both the sample temperature and level of crystallinity.[2-4] In particular, it was concluded from the

---

[1] This work was supported by the National Aeronautics and Space Administration under Research Grant NSG 247-62 to Florida State University.

[2] R. Kitamaru, L. Mandelkern, and J. Fatou, *J. Polymer Sci.*, **2B**, 511 (1964).

[3] R. Kitamaru and L. Mandelkern, *J. Am. Chem. Soc.*, **86**, 3529 (1964).

[4] T. Okada and L. Mandelkern, Abstracts, International Symposium on Macromolecular Chemistry, Tokyo, 1966; *J. Polymer Sci.*, in press.

partitioning between sol and gel of samples identically irradiated at 130–133° that the efficiency of cross-linking of crystalline polyethylene was twice that for a molten or completely amorphous sample.[2,3] It was further determined that $G(H_2)$ was only weakly dependent on the level of crystallinity, implying that the state-dependent cross-linking mechanism proceeds without hydrogen evolution. This avenue for cross-linking implicates end groups in the reactions involved[5] since there is one vinyl end group per molecule for the type of polyethylene usually studied. The role of vinyl groups in highly crystalline samples cannot be appropriately studied by examining fractions of increasing molecular weight inasmuch as the crystallinity content of linear polyethylene above 2–3 × 10^5 is sharply reduced.[6,7] Completely amorphous and highly crystalline samples of high molecular weight could not be contrasted, therefore, under identical irradiation conditions.

To circumvent this difficulty we have removed the vinyl end group from a lower molecular weight sample by hydrogenation.[8] The hydrogenation was performed on a molecular weight fraction having a viscosity-average molecular weight[6] of 6.1 × 10^4. The concentration of vinyl end groups in this sample was 2.17 × 10^{-5} mole/g, which corresponds to a number-average molecular weight of 4.6 × 10^4. After hydrogenation, the viscosity-average molecular weight remained unchanged. The infrared absorption band at 908 cm^{-1}, typical of the vinyl group, had completely disappeared. Both a hydrogenated and unhydrogenated sample was isothermally crystallized from the melt at 130° for 25 days and then slowly cooled to room temperature. The densities of the samples were 0.980 and 0.981 and the enthalpies of fusion were 58.5 and 60.4 cal/g, respectively. These values correspond to a crystalline fraction of about 0.90[6,7] and indicate that both the hydrogenated and unhydrogenated samples possessed identical crystallinity properties.

A comparison of the results of irradiating these samples at 130° in both the highly crystalline and completely molten (amorphous) states is summarized in Table I. For the nonhydrogenated control sample the results are virtually identical with those previously reported.[2-4] The critical dosage required for gelation is about twice as great for the completely amorphous sample as compared to the highly crystalline one. On the other hand, for the hydrogenated sample treated in exactly the same manner, the highly crystalline sample required a slightly higher critical dose for gelation than did the completely amorphous polymer. It becomes clear, therefore, that the greater efficiency of cross-linking in the nonhydrogenated highly crystalline sample must result from reactions involving the vinyl end group. This would be an additional unique cross-linking reaction resulting from irradiation, which involves the vinyl end group in the highly crystalline polymer and does not necessarily require the production of hydrogen. The importance of the vinyl end group in the chemical acts involved and in the possible alteration of the molecular weight distribution have been pointed out by Dole and collaborators.[5,9] Since the end groups are excluded from the crystal lattice,[10] the effective vinyl group concentration is much greater than the nominal concentration. The $G(H_2)$ values for the two highly crystalline polymers are virtually the same. On the other hand, we note that the $G(H_2)$ value of 6.2 for the completely amorphous hydrogenated samples is identical with the asymptotic value obtained for nonhydrogenated high molecular weight material.[4]

Table I. Results of the Irradiation of Hydrogenated and Nonhydrogenated Polyethylene at 130°[a]

Sample		R_c[b]	$G(H_2)$[c]
Nonhydrogenated	Completely amorphous	3.1	5.4
	Highly crystalline	1.6	5.6
Hydrogenated	Completely amorphous	4.2	6.2
	Highly crystalline	4.5	5.7

[a] M_η = 6.1 × 10^4, M_n = 4.6 × 10^4. [b] Critical dosage in Mrads for gelation at 130°. [b] G value for hydrogen evolution at 130° for irradiation dose of 1.7 Mrads.

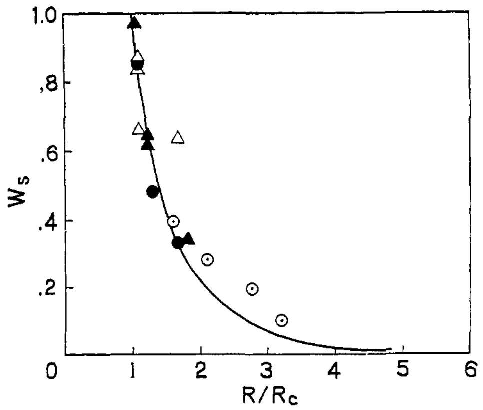

Figure 1. Plot of W_s against the ratio of the radiation dose to the critical dosage required for incipient gelation. Irradiation was carried out at 130°. Nonhydrogenated sample highly crystalline, ○; completely amorphous, ●. Hydrogenated sample highly crystalline, △; completely amorphous, ▲.

In Figure 1 we have plotted the weight fraction sol, W_s, as a function of the ratio of the radiation dose to the critical dosage for gelation. The solid line is calculated according to the theoretical relation[11,12]

$$\frac{-\ln W_s}{1 - W_s} = \frac{R}{R_c} \qquad (1)$$

which is applicable to the cross-linking of molecular weight fractions in the absence of chain scission. Except for the nonhydrogenated highly crystalline sample, the data are in very good accord with the theoretical expectations and rule out any complication from chain scission and intramolecular cross-linking during the

---

(5) M. Dole, D. C. Milner, and T. F. Williams, *J. Am. Chem. Soc.*, **79**, 4809 (1957); 80, 1580 (1958).

(6) J. Fatou and L. Mandelkern, *J. Phys. Chem.*, **69**, 417 (1965).

(7) L. Mandelkern, *J. Polymer Sci.*, **15C**, 129 (1966).

(8) The hydrogenation, in decalin solution using a rhodium on carbon catalyst, was performed for us by Dr. T. W. Brooks, of Peninsular ChemResearch, Inc. The assistance of Dr. Brooks is gratefully acknowledged.

(9) M. Dole, M. B. Fallgatter, and K. Katsuuro, *J. Phys. Chem.*, **70**, 62 (1966).

(10) L. Mandelkern, "Crystallization of Polymers," McGraw-Hill Book Co., Inc., New York, N. Y., 1964.

(11) P. J. Flory, *J. Am. Chem. Soc.*, **63**, 3096 (1941).

(12) W. H. Stockmayer, *J. Chem. Phys.*, **12**, 125 (1944).

irradiation.[13] The deviations observed at the higher dosages for the nonhydrogenated, highly crystalline polymer can be attributed to there being more than one cross-linking reaction with a retardation developing in the production of gel as the concentration of vinyl groups becomes depleted.

We can conclude that the enhanced cross-linking efficiency that is observed in the usual crystalline polyethylene is a real effect and not a consequence of any experimental artifacts.[13] The close similarity in cross-linking efficiency between the crystalline and amorphous polymer in the absence of the vinyl end group indicates that this enhancement is a unique and specific chemical effect and would not be generally expected in other crystalline polymers.

(13) M. Dole and K. Katsuura, *J. Polymer Sci.*, **3B**, 467 (1965).

T. Okada, L. Mandelkern, R. Glick
Department of Chemistry and Institute of Molecular Biophysics
Florida State University, Tallahassee, Florida 32306

Received April 26, 1967

The Crystal Structure of Twinned Tetrarhodium Dodecacarbonyl[1,2]

Sir:

Although the molecular structures of $Co_4(CO)_{12}$[3] and $Ir_4(CO)_{12}$[4] have recently been completely characterized in the solid state, little structural information has been reported for the presumed tetranuclear metal carbonyl of the congener element rhodium. A structure similar to that of $Co_4(CO)_{12}$ was suggested by Beck and Lottes[5] for the reddish orange $[Rh(CO)_3]_n$ (first prepared by Hieber and Lagally[6]) on the basis of its volatility, diamagnetism, and the resemblance of its *solution* infrared spectrum with that of $Co_4(CO)_{12}$. A three-dimensional X-ray investigation of the rhodium complex was undertaken in order to establish its tetrameric character and to ascertain the relationship of its structure to those of the stereochemically dissimilar $Co_4(CO)_{12}$ and $Ir_4(CO)_{12}$. Our interest in obtaining unambiguous molecular parameters for this complex in the *solid* state has been stimulated by recent work concerning the possible intramolecular rearrangement of $Co_4(CO)_{12}$ in solution.[7-9] All initial attempts to determine the crystalline structure of $Rh_4(CO)_{12}$ were unsuccessful owing to twinning and/or disorder of a different nature from that in the disordered crystalline structure of $Co_4(CO)_{12}$.[3a] Our continued effort to resolve this problem, however, has now provided the conclusive results reported here.

The rhodium tricarbonyl complex was synthesized by the high-pressure carbonylation of anhydrous $RhCl_3$ with freshly reduced copper as halogen acceptor.[6] A large number of optically acceptable crystals, obtained by recrystallization from several organic solvents, were examined by X-ray diffraction photographs before crystallographically suitable crystals were found; these crystals invariably showed D_{2h}-mmm Laue symmetry. The resultant orthorhombic unit cell has lattice dimensions $a = 9.24$ A, $b = 12.02$ A, $c = 17.74$ A; $\rho_{obsd} = 2.58$ g cm^{-3} *vs.* $\rho_{calcd} = 2.52$ g cm^{-3} based on four $Rh_4(CO)_{12}$ species per cell. Systematic absences of l odd for $\{h0l\}$ and k odd for $\{0k0\}$ indicate a c glide and a 2_1 axis in the b direction.

Three-dimensional film data were collected with Mo Kα radiation from two tiny crystals from which 962 independent intensity maxima corresponding to one octant of the reflection sphere were obtained. Attempts to interpret a three-dimensional sharpened Patterson function in terms of any orthorhombic space group involving either or both of the above symmetry elements were unsuccessful. Instead the only trial model which conformed to the above symmetry and Patterson vector requirements (and which later was confirmed by least-squares refinement) was based on an incoherent twinning mechanism involving a monoclinic single crystal of symmetry $P2_1/c$ and β angle of 90°. The presence of either a (100) or (001) twin mirror plane operating on the reciprocal lattice of this monoclinic unit cell would give rise to the same apparent unit cell for the twinned composite and thereby would result in the observed pseudo-orthorhombic diffraction symmetry with no streaking.[10,11]

The determination of the carbonyl positions in this twinned crystal was accomplished by successive Fourier syntheses for which application of derived mathematical relations[12] permitted a breakdown of the observed orthorhombic $|F(hkl)_o|^2$ data for the twinned composite into the $|F(hkl)_{o'}|$ and $|F(\bar{h}kl)_{o'}|$ coefficients for the monoclinic single crystal component. This Fourier analysis was compicated by the fact that the initial atomic coordinates obtained for the crystallographically

---

(1) Research jointly sponsored by the National Institutes of Health and the U. S. Atomic Energy Commission under contract with the Union Carbide Corporation, and by the National Science Foundation (GP 4919) at the University of Wisconsin.

(2) Presented in part by C. H. Wei at the National Meeting of the American Crystallographic Association, Minneapolis, Minn., Aug 20–25, 1967.

(3) (a) C. H. Wei and L. F. Dahl, *J. Am. Chem. Soc.*, 88, 1821 (1966); (b) P. Corradini, *J. Chem. Phys.*, 31, 1676 (1959); P. Corradini and A. Sirigu, *Ric. Sci.*, **36**, 188 (1966).

(4) G. R. Wilkes, Ph.D. Thesis, University of Wisconsin, Madison, Wis., 1965; G. R. Wilkes and L. F. Dahl, to be published.

(5) W. Beck and K. Lottes, *Chem. Ber.*, **94**, 2578 (1961).

(6) W. Hieber and H. Lagally, *Z. Anorg. Allgem. Chem.*, **251**, 96 (1943).

(7) F. A. Cotton, *Inorg. Chem.*, **5**, 1083 (1966).

(8) H. Haas and R. K. Sheline, *J. Inorg. Nucl. Chem.*, **29**, 693 (1967).

(9) E. A. C. Lucken, K. Noack, and D. F. Williams, *J. Chem. Soc., Sect. A*, 148 (1967).

(10) Since completion of our structural analysis, we have learned from private correspondence (1967) that Dr. W. Murayama of the Central Laboratories of Ajinomoto Co., Inc. (Kawasaki, Japan), has also carried out an X-ray study of $Rh_4(CO)_{12}$. Although his attempts to unravel the carbonyl atomic positions from Fourier maps were unsuccessful, it is noteworthy that his interpretation of the orthorhombic crystal data was based on an identical monoclinic twinning model of symmetry $P2_1/c$.

(11) For either a (100) or (001) twinning plane the two enantiomorphous monoclinic reciprocal lattices (with $\beta^* = 90°$) superimpose so that the observed and calculated intensities, $|F(hkl)_o|^2$ and $|F(hkl)_c|^2$, for the pseudo-orthorhombic reciprocal lattice of the twinned composite are related to the corresponding quantities of the monoclinic reciprocal lattice, $|F(hkl)_{o'}|^2$ and $|F(\bar{h}kl)_{o'}|^2$ and $|F(hkl)_{c'}|^2$ and $|F(hk\bar{l})_{c'}|^2$, by the following relationships

$$|F(hkl)_o|^2 = m|F(hkl)_{o'}|^2 + (1 - m)|F(\bar{h}kl)_{o'}|^2$$

$$|F(hkl)_c|^2 = m|F(hkl)_{c'}|^2 + (1 - m)|F(\bar{h}kl)_{c'}|^2$$

where m represents the fraction of one monoclinic component lattice. Since the symmetry of the twinned composite is orthorhombic within experimental error, m must be approximately 0.5. A value of $m = 0.504 \pm 0.009$ was obtained when m was refined as a variable parameter by least squares.

(12) In order to estimate magnitudes of the monoclinic structure factors, $F(\bar{h}kl)_{o'}$ and $F(\bar{h}kl)_{o'}$, the observed orthorhombic $|F(hkl)_o|^2$ was apportioned as follows.

$$|F(hkl)_{o'}| = \left[|F(hkl)_o|^2 \frac{|F(hkl)_{c'}|^2}{|F(hkl)_c|^2}\right]^{1/2}$$

$$|F(\bar{h}kl)_{o'}| = \left[|F(hkl)_o|^2 \frac{|F(\bar{h}kl)_{c'}|^2}{|F(hkl)_c|^2}\right]^{1/2}$$