

AN INVESTIGATION OF THE ELECTRICAL CONDUCTIVITY OF STEROIDS

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ABSTRACT The electrical conductivity of sixteen steroids in the solid state was measured as a function of temperature. While too small to measure at room temperature, the exponential increase in conductivity with temperature can be determined at elevated temperatures (70° – 130°C). Most steroids tested had a conductivity of 10^{-18} to 10^{-15} $ohm^{-1} cm^{-1}$ at 100°C and an activation energy of 2 to 4 *ev*. It is concluded that the observed conductivity is due to impurities. Exposure of keto steroids to iodine vapor results in unstable colored compounds, probably charge transfer complexes, which in some cases have a conductivity as high as 10^{-4} $ohm^{-1} cm^{-1}$.

INTRODUCTION

The electrical conductivity of steroids is of interest because of its possible involvement in electron transport in biological systems (Szent-Györgyi, 1960). The steroids are good insulators, yet their conductivity is sufficiently high at elevated temperatures so that it can be determined over a substantial range of conductivity. It was found that the conductivity of the steroids tested increases exponentially with temperature, as is usually found with organic compounds. The conductivity of organic compounds is frequently explained in terms of mobile pi electrons (Garrett, 1959). One question to be investigated is whether steroids having conjugated double bonds exhibit substantially higher conductivity than steroids without conjugated double bonds. Another is the role of impurities.

MEASUREMENTS OF UNDOPED SAMPLES

Most of the steroids used for this experiment were in the powder form supplied by the manufacturer,¹ but some were purified first by vacuum sublimation. The powder samples were compressed into disks (about 3 mm diameter, 2 mm thick) and electrodes applied (usually silver paint). Measurements of the electrical resistivity of these disks as a function of temperature were carried out in a temperature-controlled

¹ Most steroids had a melting point range of 1°-2°C, and were obtained from Steraloids, Inc., Flushing, New York.

box through which dry nitrogen was flushed. Spot checks were made of the sample current as a function of voltage and it was found that Ohm's law was obeyed, as expected, at the moderate fields used (about 10^3 v/cm).

During the initial heating cycle, the conductivity of the steroid samples was quite irreproducible, but upon prolonged heating (about 10 hours at 100°C), the conductivity decreased to a constant value which was reproducible on both heating and cooling cycles. The observed conductivity (σ) can be described by the formula $\sigma = \sigma_0 e^{-E_a/KT}$ from which the activation energy (E_a) can be found.

In Fig. 1, the temperature dependence of the conductivity of several steroids is

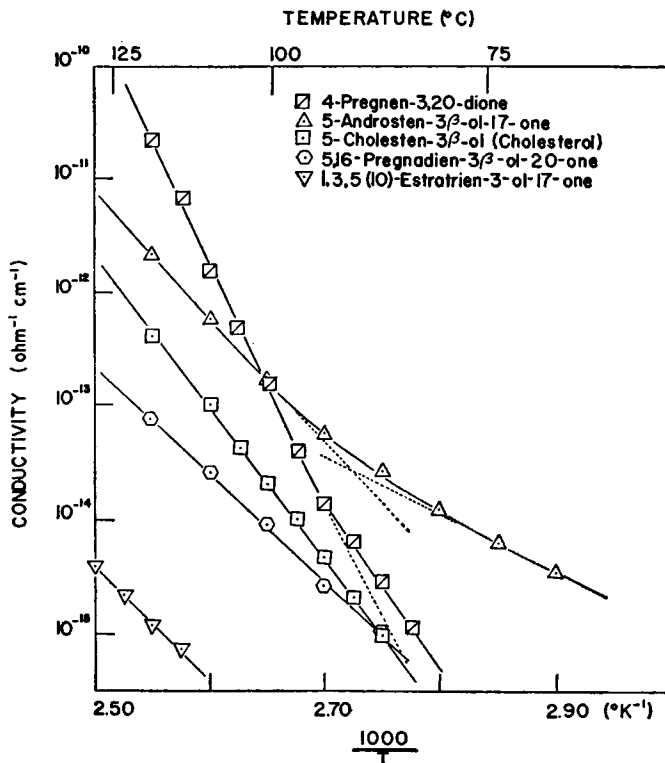


FIGURE 1 Electrical conductivity (log scale) of several undoped steroids as a function of reciprocal temperature. The conductivity increase with temperature of cholesterol is typical of most steroids tested.

shown. These steroids were selected to represent the range of behavior observed. In a few cases a break to a lower slope typical of impurity conductivity was found (*i.e.* 5-androsten- 3β -ol-17-one), but it was not reproducible from sample to sample. Samples purified by vacuum sublimation have somewhat lower conductivities and higher activation energies. The slope corresponding to the higher activation

energies also depended on how the sample was prepared; variations of 10 per cent or more were common. In one case (5 α -androstan-3 β -ol-17-one, see Table I), the conductivity across three pairs of crystal faces of a single crystal could be measured and was found to be anisotropic. The conductivity perpendicular to the flat face was over 100 times greater than the two other directions.

Some representative results of measurements of the conductivity as a function of temperature are given in Table I to serve as a guide to future work. The activa-

TABLE I
ELECTRICAL CONDUCTIVITY OF SEVERAL STEROIDS

Steroid	Conductivity	E_a
	at 100°C	
	<i>ohm⁻¹ cm⁻¹</i>	<i>ev</i>
1, 4-Androstadien-3, 17-dione	10 ⁻¹⁴	3.0-4.5 (2.3)*
5 α -Androstan-3, 17-dione	10 ⁻¹⁸	3.2
5 β -Androstan-3, 17-dione	10 ⁻¹⁸	3.0
	10 ⁻¹⁶ ‡	3.2‡
5 α -Androstan-3 β -ol-17-one	10 ⁻¹⁸	2.0
	10 ⁻¹⁷ ‡, \perp	1.8‡
	10 ⁻¹⁹ ‡, \parallel	—
5 α -Androstan-17 β -ol-3-one	2 × 10 ⁻¹⁸	2.2
4-Androsten-3, 17-dione	5 × 10 ⁻¹⁶	2.9
4-Androsten-17 β -ol-3-one (testosterone)	2 × 10 ⁻¹⁴	2.9
5-Androsten-3 β -ol-17-one	3 × 10 ⁻¹⁴	2.5
5 β -Cholanic acid-3 α , 7 α , 12 α -triol (cholic acid)	10 ⁻¹⁶	2.8
	10 ⁻¹⁶ ‡	3.0‡
5-Cholesten-3 β -ol (cholesterol)	10 ⁻¹⁴	2.4
5, 7, 22-Cholestatrien-24 β -methyl-3 β -ol (ergosterol)	2 × 10 ⁻¹⁸	2.2
1, 3, 5(10)-Estratrien-3, 17 β -diol (17 β -estradiol)	<10 ⁻¹⁷	—
1, 3, 5(10)-Estratrien-3-ol-17-one (estrone)	10 ⁻¹⁶	2.2
	<10 ⁻¹⁷ ‡	—
4-Pregnen-3, 20-dione (progesterone)	10 ⁻¹⁸	3.3-4.6 (2.1)*
4-Pregnen-11 β , 17 α , 21-triol-3, 20-dione	<10 ⁻¹⁷	—
5-Pregnen-3 β -ol-20-one (pregnenolone)	10 ⁻¹⁸	2.1

* A wide range of activation energies was observed from sample to sample; a value in parenthesis refers to a second activation energy found at a lower temperature.

‡ Single crystal results, extrapolated to 100°C.

tion energies are all surprisingly high. Organic semiconductors with activation energies over 2 eV are rare (note that the activation energy has not been multiplied by two so as to express it as an energy gap). The problem of explaining how the charge carries with such a high activation energy (and a reasonably low mobility) can be thermally activated is more severe for the steroids than for most other organic semiconductors (Nelson, 1963). It may be necessary to invoke some sort of non-equilibrium process. The usual models for intrinsic conductivity do not fit.

Steroids possessing double bonds do not have strikingly higher conductivities or lower activation energies. Indeed, no obvious correlation with chemical composition was found. This fact, together with the occasional presence of more than one activation energy, the variability of the results with sample preparation, and the decrease in conductivity with further purification leads to the conclusion that the observed conductivity is due to impurities. Presumably then, the conductivity of a pure steroid would be much less than 10^{-18} ohm $^{-1}$ cm $^{-1}$ at room temperature.

CONDUCTIVITY OF STEROID-IODINE COMPLEXES

If the accidental presence of small amounts of impurities can cause the observed conductivity, it seemed likely that larger amounts of selected impurities would result in a much higher conductivity. Iodine was chosen as a doping agent because of its apparent ability to form charge transfer complexes with certain steroids (Szent-Györgyi, 1960; Heller, Hohensee, and Huttenrauch, 1958). Charge transfer complexes of large aromatic molecules with iodine (*e.g.* perylene—I₂) are known to have high conductivities (Inokuchi and Akamatu, 1961; Briegleb, 1961). As can be seen from Fig. 2, some steroid-iodine complexes have a high conductivity, many orders of magnitude higher than the undoped steroids.

The steroid-iodine complexes were made simply by exposing the steroids to iodine vapor at room temperature. Normally, the reaction was carried out in air, but it also occurred under dry nitrogen. As the iodine was absorbed, the steroids changed color (violet, orange, brown, or black) and the conductivity increased. The reaction is at least partly reversible since the conductivity decreases and the color removed by exposing to an iodine-free atmosphere for a time.

Steroids containing keto groups formed the darkest and most conducting complexes. The keto oxygen may act as a local electron donor which can transfer electrons to an iodine molecule presumably absorbed nearby. The conductivity and color changes in the other types of steroids may be due to small amounts of keto steroid impurities. For example, a black conducting complex was produced using cholesterol which had been oxidized in air to form products containing keto steroids (as identified by the Lifschutz test, Fieser and Fieser, 1959) while purified cholesterol showed little reaction.²

The high conductivity of the steroid-iodine complexes adds support to the idea of Szent-Györgyi that steroids may function in a biological system as an electron transmitter between molecules. Although a charge transfer complex of a steroid with a biologically important molecule has not yet been conclusively demonstrated,³

² It is interesting to note the suggested connection between charge transfer complexes and carcinogenesis (Allison and Nash, 1963; Pullman and Pullman, 1963). Oxidation products of cholesterol are carcinogenic and like many carcinogens, form charge transfer complexes.

³ Molinari and Lata (1962) have observed an interaction with pyrimidines and purine derivatives which they correlate with electron donor-acceptor strength.

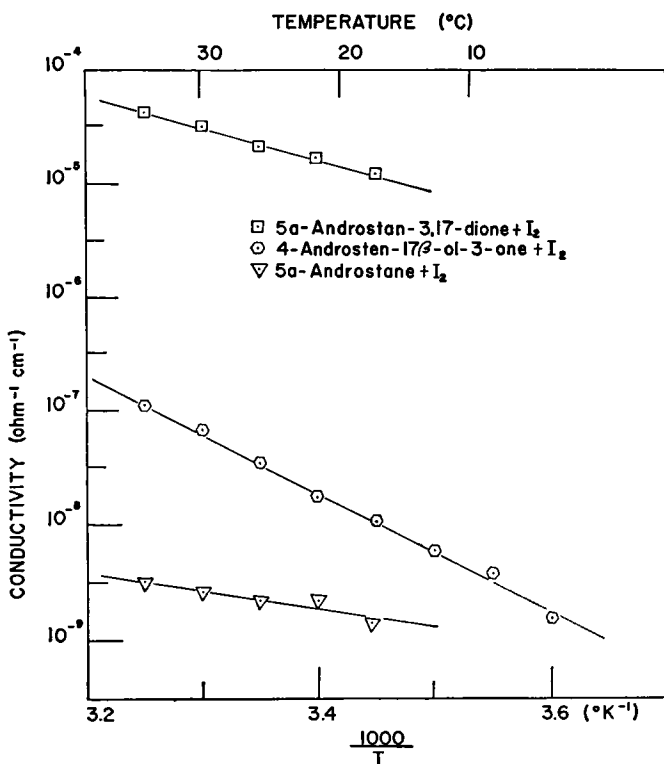


FIGURE 2 Electrical conductivity (log scale) of several steroid-iodine complexes as a function of reciprocal temperature. The weight of iodine absorbed corresponds to about 1 molecule of I_2 per 10 to 1000 steroid molecules.

it is possible to prepare complexes of steroids with molecules other than iodine (Allison and Nash, 1963).

We wish to thank Dr. David Harker for many helpful discussions. Credit is due to Mr. William Wilson for the construction of much of the equipment used and to Mr. Joel Sundquist for assistance in data collection.

This work was supported in part by Public Health Service Research Grant CA06183 from the National Cancer Institute.

Received for publication, January 14, 1964.

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