and Nutting.[3] Salts of the highest purity were used and standard methods of analysis were followed in the determination of the changes in silver content of cathode, anode and middle portions. The results obtained in four experiments are reported in Table I.

TABLE I

DATA FOR THE MIGRATION OF SILVER IN SOLUTIONS OF SODIUM THIOSULFATE PRACTICALLY SATURATED WITH SILVER CHLORIDE AT 25°

No. of experiment	1	2	3	4
Weight Ag in coulometer, g.	0.0739	0.0523	0.0514	0.0504
Moles $Na_2S_2O_3$ per liter	.0976	.1000	.1034	.0967
Equivalents Ag per liter	.0795	.0808	.0843	.0787
Loss Ag at cathode, g.	.0150	.0111	.0126	.0093
Gain Ag at anode, g.	.0165	.0109	.0101	.0123
Average transport number of Ag^+	−.213	−.210	−.221	−.215
Ratio equivalents of $AgS_2O_3^-$ to total number equivalents	.204	.202	.204	.204

The changes in the anode and cathode portions were of the order of 2 to 3% of the original silver content. The changes in the middle portion were equal to zero within the limits of accuracy of the analysis. The numbers in the last line of the table were obtained on the assumption that the whole amount of silver is combined as $AgS_2O_3^-$; the total number of equivalents refers to all ionic species actually present (for instance, in experiment No. 2 we have 0.2 Na^+ + 0.0808 $AgS_2O_3^-$ + 0.0384 $S_2O_3^=$ + 0.0808 Cl^-).

Averaging the results of the four experiments we may say that a 0.1 molar solution of sodium thiosulfate saturated with silver chloride at 23° contains 0.08 equivalent of silver per liter and that the transport number of Ag^+ in such a solution is −0.215 at 25°.

(3) Van Rysselberghe and Nutting, THIS JOURNAL, 55, 996 (1933).

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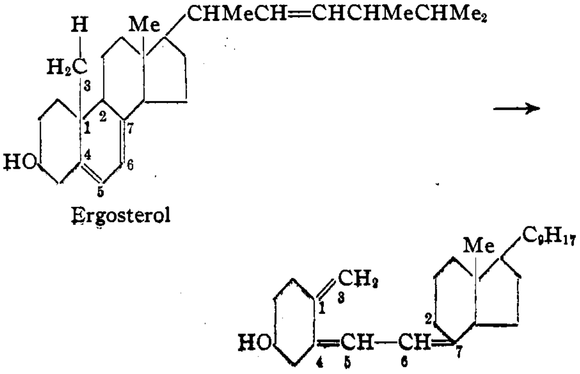
Calculation of the Activation Energy of the Rearrangement of Ergosterol to Calciferol

BY J. R. OWEN AND ALBERT SHERMAN

According to the work of Windaus and Grundmann[1] and of Heilbron, Jones, Samant and Spring[2] the rearrangement of ergosterol to calciferol may be represented by the equation



Ergosterol

Calciferol

This change involves the breaking of the 1,2-carbon–carbon bond and a shift of a hydrogen atom from carbon atom 3 to carbon atom 2, with the subsequent formation of a double bond between carbon atoms 1 and 3.

We have constructed molecular models and calculated the activation energy for the probable mechanism of such a transformation according to the semi-empirical method of Eyring.[3] The constants for the Morse curves used in the calculations are given in Table I.

TABLE I

Bond	r_0, Å.	ω_0 cm.$^{-1}$	D, kcal.
C–C	1.54[a]	990[b]	83.0[c]
	1.46[d]	[e]	74.5[f]
	1.44[g]	990[b]	74.5[f]
C–H	1.12[h]	2930[c]	92.3[h]

[a] Pauling, *Proc. Nat. Acad. Sci.*, **18**, 293 (1932). [b] Mecke, *Z. physik. Chem.*, **17B**, 1 (1932). [c] Pauling, THIS JOURNAL, **54**, 3570 (1932). [d] This value is the average of the C–C distances in a single and a double bond, and was used as the final 1,3-carbon–carbon distance. [e] This value was not needed since no Morse curve was drawn for this bond. [f] This value is one-half the strength of the carbon–carbon double bond and was used in all activation energy calculations involving the final 1,3-carbon–carbon bond, as well as in the construction of the Morse curve for the C–C bond in the ring broken. [g] This value is the carbon–carbon distance in benzene and was used in the construction of the Morse curve for the C–C bond in the ring broken. [h] Mulliken, *Rev. Modern Phys.*, **4**, 1 (1932).

According to Steenbock and co-workers[4] the long wave length limit for the conversion of ergosterol into calciferol by ultraviolet irradiation is 3100 Å. This corresponds to an energy of

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(1) Windaus and Grundmann, *Ann.*, **524**, 295–99 (1936).

(2) Heilbron, Jones, Samant and Spring, *J. Chem. Soc.*, 905–907 (1936).

(3) See, *e. g.*, the article by Van Vleck and Sherman, *Rev. Modern Phys.*, **7**, 167 (1935).

(4) Steenbock and co-workers, *J. Biol. Chem.*, **63**, 25 (1925).

approximately 92 kcal. and represents a maximum value of the activation energy, since some of the energy absorbed may be dissipated as heat.

We have considered many mechanisms for this rearrangement and the value which we calculate for the transformation involving the lowest activation energy is 72 kcal. The mechanism of this rearrangement will be described in some detail.

Initially the carbon atoms 1, 2 and 3 and the hydrogen atom taking part in the reaction are in the same plane. The C–H group rotates about the 1,3-carbon–carbon bond until the three carbon atoms are at the corners of an equilateral triangle with the hydrogen atom equidistant (approximately 1.12 Å.) from carbon atoms 2 and 3. Up to this point all four atoms remain in the same plane. The next three steps occur simultaneously: (1) the hydrogen atom moves away from carbon atom 3, at the same time maintaining a constant distance from carbon atom 2; (2) carbon atoms 1 and 2 separate to a distance of approximately 2.07 Å.; and (3) the two parts of the molecule formed by the breaking of the 1,2-carbon–carbon bond rotate about the 5,6-carbon–carbon bond so that the plane of carbon atoms 2, 6 and 7 is at an angle of approximately 26° with that of the carbon atoms 1, 4 and 5. Following these steps the hydrogen atom moves to a final position determined by the ring of which carbon atom 2 is a part, and by the valence angles of this carbon atom. The system is now in the activated state and from this point onward (that is, as the rotation about the 5,6-carbon–carbon bond continues) the energy of the system decreases.

There are two factors which we have not considered that will affect the energy required for activation. The double bond which is formed between carbon atoms 1 and 3 is part of a conjugated system (atoms 3,1,4,5,6,7) and, although quantitative calculations have not been made, we know that this will tend to lower the activation energy slightly. The large size of the molecule introduces steric factors which probably will cause an increase in the activation energy. These two factors will tend to cancel each other, and we have not attempted to estimate them quantitatively. Their effect will not be large.

From the nature of the rearrangement it is evident that another mechanism could involve the breaking of a C–H bond (92.3 kcal.) and a reaction of the H atom with carbon atom number 2. This mechanism would therefore involve an energy of 92.3 kcal., and hence we conclude that the activation energy for the conversion of ergosterol to calciferol lies between 72 and 92 kcal. This is consistent with the value found by Steenbock for the long wave length limit.

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A Simple Method for the Preparation of the Chloro Ketone $C_{19}H_{27}OCl$, Dehydroandrosteryl Chloride

BY EVERETT S. WALLIS AND E. FERNHOLZ

In a recent paper by A. Butenandt and W. Grosse[1] the statement is made that replacement of the hydroxyl group in dehydroandrosterone by chlorine by the usual methods is unsatisfactory, low yields of the chloro ketone being obtained. From what is written one gets the impression that the difficulties involved are, indeed, serious, for the authors considered other possibilities and developed a new method which involves the following steps

Dehydroandrosterone ⟶ toluenesulfonate (71%) ⟶
epi-dehydroandrosterone methyl ether[2] (99%) ⟶
dehydroandrosteryl chloride (79%); yield over all (56%)

As is readily seen the yield of the chloride is not too satisfactory and even if we could consider the yield as fair the method would still be involved.

In the course of some of our experiments we have had occasion also to prepare this important chloro ketone. In our hands the treatment of dehydroandrosterone with phosphorus pentachloride has always given very satisfactory results. When the reaction is carried out in chloroform solution the yield is 83%, and the preparation involves but one step.

Experimental Part

One gram of dehydroandrosterone was added to a mixture of 10 cc. of dry chloroform and 1 g. of phosphorus

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[1] A. Butenandt and W. Grosse, *Ber.*, **69**, 2776 (1936).

[2] The experimental results of Wallis, Fernholz and Gephart [THIS JOURNAL, **59**, 137 (1937)] obtained in a study of the action of potassium acetate on cholesteryl *p*-toluene-sulfonate show that a molecular rearrangement takes place during this reaction. In the light of these experiments the naming of this methyl ether may not be justified. It is entirely possible that the compound may have a different structure.