of 2,4,4-trimethylpentene-2) to yield isoöctane (2,4,4-trimethylpentane), the assumption was made that mixtures of this paraffin with the parent olefins formed practically "perfect" solutions. Accordingly such solutions should be formed from the components without any appreciable heat of mixing and the partial vapor pressures of the components should follow Raoult's law. In view of the structural similarity of the paraffins and the olefins here involved, this assumption of perfect solutions certainly appeared reasonable on *a priori* grounds. Moreover, Beatty and Calingaert[2] had shown that the total pressures of mixtures of *n*-heptane and *n*-heptene-3 near the boiling point do not exhibit at any concentration more than a 0.5% positive deviation from the requirements of Raoult's law. However, the departure from ideality of such solutions may be appreciably greater at lower temperatures. In view of this possibility and the simplicity of the measurements, we decided to make also some direct calorimetric determinations of the heats of mixing of diisobutylene and isoöctane.

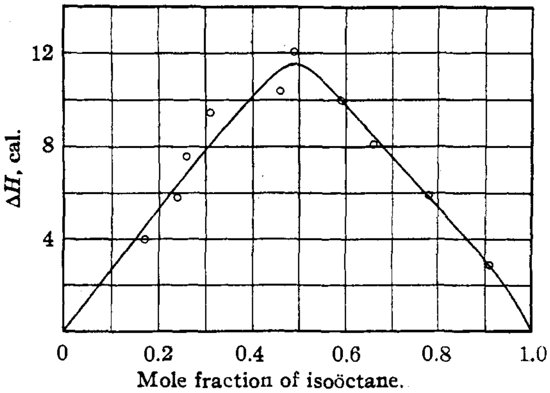

Fig. 1.—The heat absorption per mole of solution formed plotted against the mole fraction of isoöctane.

The vacuum jar calorimeter and the method of mixing employed previously by Parks and Chaffee[3] were used again in the present study. The mixing took place at 23° and the temperature change on formation of the solutions was measured to 0.001° by a copper–constantan thermocouple in conjunction with a White potentiometer. The necessary specific heat data for isoöctane and diisobutylene were taken from previous studies[4] in this Laboratory. Our hydrocarbon samples were carefully prepared materials which had been presented to us by the Shell Development Company. They had boiling ranges of about a degree and crystallized completely when cooled with liquid air; the respective densities at 20° were 0.6912 for the isoöctane and 0.7168 for diisobutylene.

Ten separate determinations of the heat of mixing were made in forming solutions ranging from 0.17 to 0.91 mole fraction of isoöctane. In the isothermal mixing process there appeared, for all concentrations, a small endothermic effect, which we have represented graphically in the accompanying figure. In our experiments this heat absorption reached a maximum for the formation of a solution containing 0.49 mole fraction of the isoöctane. In this case we found $\Delta H_{296} = 12.1\ (\pm 1.0)$ cal. for the process

$$0.49\ C_8H_{18}(l) + 0.51\ C_8H_{16}(l) = 1 \text{ mole of solution}$$

The minuteness of such a heat effect can be further emphasized by noting that it is only 1.3% of the effect previously recorded in the formation of a comparable solution of benzene and *n*-hexane.[5]

The previous assumption that such diisobutylene–isoöctane solutions are practically perfect is thus well justified.

[2] H. A. Beatty and G. Calingaert, *Ind. Eng. Chem.*, **26**, 505 (1934).

[3] G. S. Parks and C. S. Chaffee, *J. Phys. Chem.*, **31**, 439 (1927).

[4] G. S. Parks, H. M. Huffman and S. B. Thomas, THIS JOURNAL, **52**, 1032 (1930); G. S. Parks and H. M. Huffman, *ibid.*, **52**, 4381 (1930).

[5] "International Critical Tables," Vol. V, page 157.

DEPARTMENT OF CHEMISTRY
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The Transport Number of Silver in Solutions of Sodium Thiosulfate Practically Saturated with Silver Chloride

BY PIERRE VAN RYSSELBERGHE AND S. M. KNAPP

Evidence obtained by Müller and by Carrière and Raulet[1,2] from electrometric titration and conductivity shows that in aqueous mixtures of sodium thiosulfate with a silver salt, the silver is present as a monovalent anion $AgS_2O_3^-$.

We have obtained direct evidence for the existence of such an ion by measuring the transport number of silver in solutions of sodium thiosulfate saturated with silver chloride at 23°. The experiments were run at 25° according to a technique similar to that of Van Rysselberghe

[1] Müller, *Z. anorg. Chem.*, **133**, 202 (1924).

[2] Carrière and Raulet, *Compt. rend.*, [7] **192**, 423 (1931).

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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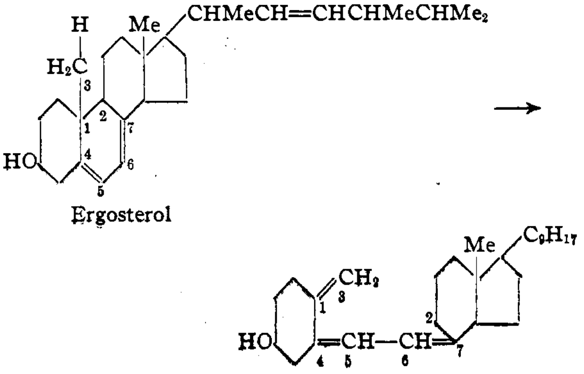
RECEIVED JANUARY 19, 1937

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).