dehydration products have been reported from each alcohol. In view of the fact that methyl acetylechinocystate has been dehydrated through the methanesulfonyl derivative under very mild conditions and that the process does not appear to involve rearrangement,[1] it seemed desirable to try this method of dehydration on the amyrins. If no rearrangement took place, the product formed should indicate which of the above dienes are primary products and which are rearranged products.

Mesyl α-amyrin was prepared from α-amyrin and methanesulfonyl chloride in pyridine. It was crystallized from methanol and decomposed at 116–118°.

Anal.[2] Calcd. for $C_{31}H_{52}O_3S$: C, 73.75; H, 10.39. Found: C, 73.97; H, 10.28.

After a solution of mesyl-α-amyrin in methanol containing hydrochloric acid was refluxed, only a glassy solid was isolated which could not be crystallized. When solid mesyl-α-amyrin was heated at 90°, it gradually decomposed, and pure α-amyradiene-III,[3] m. p. 193–194°, was isolated from the products. This compound very likely is a rearranged substance, since the methanesulfonic acid formed on decomposition subjects the product to strongly acid conditions at a fairly high temperature.

To avoid the acid conditions, mesyl-α-amyrin was refluxed in pyridine solution. The product melted at 129–131°; $[\alpha]^{20}D$ +148° in chloroform. It depressed the melting points of both α-amyradiene-I[4,5] and of α-amyradiene-II.[5,6,7] Hence it is a new dehydration product which has been named α-amyradiene-IV. It is transparent to ultraviolet light down to 220 mμ.

Anal. Calcd. for $C_{30}H_{48}$: C, 88.16; H, 11.84. Found: C, 88.45; H, 11.44.

Mesyl-β-amyrin prepared from β-amyrin and methanesulfonyl chloride in pyridine and crystallized from methanol decomposed at 127–128°.

Anal. Calcd. for $C_{31}H_{52}O_3S$: C, 73.75; H, 10.39. Found: C, 73.91; H, 10.21.

When solid mesyl-β-amyrin was heated at 105°, no pure compound could be isolated from the decomposition products. When a solution of mesyl-β-amyrin in pyridine was heated, the product was identical with β-amyradiene-II.[6,7]

It is of interest to compare the dehydration of methyl acetylechinocystate and of the amyrins. The dehydration of methyl acetylechinocystate yields the same product when the mesyl derivative is heated with acid methanol or with pyridine, or when the alcohol is heated with phosphorus pentoxide.[8] β-Amyrin gives the same product by decomposition of the benzoate by heat or of the methanesulfonate by refluxing in pyridine, but a different product under acid conditions. α-Amyrin has given a different product by almost every procedure used. Hence one may conclude that the ease of rearrangement on dehydration is echinocystic acid < β-amyrin < α-amyrin.

Which, if any, of the four α-amyradienes is a primary product is difficult to say. α-Amyradiene-II seems to be the most likely candidate since it is obtained both by the decomposition of the benzoate[6] and by the Tschugaev reaction.[7]

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[1] Frazier and Noller, THIS JOURNAL, **66**, 1267 (1944).

[2] Microanalyses by C. W. Koch, Albany, Calif.

[3] Vesterberg, *Ber.*, **24**, 3834 (1891).

[4] Vesterberg, *ibid.*, **20**, 1242 (1887).

[5] Ewen, Gillam and Spring, *J. Chem. Soc.*, 28 (1944).

[6] Winterstein and Stein, *Ann.*, **502**, 223 (1933).

[7] Dieterle, Brass and Schaal, *Arch. Pharm.*, **275**, 557 (1937).

[8] F. Alves, unpublished work at Stanford University.

Heat of Combustion and Formation of 1,3,5,7-Cyclooöctatetraene and its Heat of Isomerization to Styrene

BY EDWARD J. PROSEN, WALTER H. JOHNSON AND FREDERICK D. ROSSINI*

In 1947, the authors[1] reported the results of measurements of the heat of combustion of 1,3,5,7-cyclooöctatetraene. At that time, the quantity of material available for the investigation was very limited, being only 15 g., and it was not possible to purify the material further nor to evaluate its purity. Recently, Scott, Gross, Oliver and Huffman[2] reported the results of measurements at low temperatures on a sample of cyclooöctatetraene of high purity, 99.92 mole per cent. and gave a value for the freezing point for zero impurity and for the cryoscopic constant. From these data and the value of the freezing point of the previous sample, it is calculated that the latter contained about 5.3 mole per cent. of impurity, most probably the isomer, styrene, to which cyclooöctatetraene readily isomerizes. Such an amount of impurity, if styrene, would cause the previously reported value[1] for the heat of combustion to be too low by 0.18%. In view of this fact, a sample of the same cyclooöctatetraene of high purity measured by Huffman and coworkers[2] was obtained[3] for a redetermination of the heat of combustion. Measurements on the purer sample were made in the same manner as previously reported, with the following result for the heat of combustion, as the mean value from five experiments

$$C_8H_8(\text{liquid, cyclooöctatetraene}) + 10O_2(\text{gas}) = 8CO_2(\text{gas}) + 4H_2O(\text{liquid});\ \Delta Hc^\circ_{298.16} = -4545.92 \pm 0.90\ \text{kj./mole, or } -1086.50 \pm 0.22\ \text{kcal./mole}$$

The ± value given in the foregoing, as well as that previously reported for the heat of combustion,

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* Editorial Board 1947–.

[1] E. J. Prosen, W. H. Johnson and F. D. Rossini, THIS JOURNAL, **69**, 2068 (1947).

[2] D. W. Scott, M. E. Gross, G. D. Oliver and H. M. Huffman, *ibid.*, **71**, 1634 (1949).

[3] From the General Aniline and Film Company, New York, N. Y., through the courtesy of Dr. P. G. Stevens.

does not include the effect of impurities. The previously reported value is lower than the foregoing value by 0.16%, which difference is in excellent accord with the calculation based on 5.3 mole per cent. of styrene as impurity. In the new value, the uncertainty should be increased to ±0.30 kcal./mole to allow for the effect of impurities.

On the basis of the new value for the heat of combustion, the following values are calculated for the heat of formation and the heat of isomerization

8C(solid, graphite) + $4H_2$(gas) = C_8H_8(liquid, cyclooctatetraene); $\Delta Hf°_{298.16} = +60.82 \pm 0.32$ kcal./mole

1,3,5,7-cycloöctatetraene(liquid) = styrene(liquid); $\Delta H°_{298.16} = -36.10 \pm 0.36$ kcal./mole

The previous conclusion regarding the instability of the cycloöctatetraene ring, relative to the benzene ring, is unchanged.

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Anomalous Activation Energy in the Alkaline Hydrolysis of an Ether-ester[1]

BY BERNARD RABINOVITCH* AND CHARLES H. SCHRAMM

In the course of a study of the alkaline hydrolysis of swollen cellulose acetates, it became necessary to study the rates and activation energies of the alkaline hydrolysis of a series of simple esters. The purpose of this was to determine what effect, if any, a given group would have on the course of hydrolysis of an acetate group on a neighboring carbon atom. In this way we hoped to see how the state of substitution of a cellulose acetate chain might be expected to influence the rate of hydrolysis of its component ester groups.

Experimental

All the experiments were carried out at three temperatures between 15 and 25°. The hydrolyzing medium was a 50/50 volume/volume 0.1 *N* standard sodium hydroxide solution–acetone mixture, and the kinetics of the reactions were followed conductometrically.[2]

All the esters used were redistilled commercial products, none of which contained free acid. In all cases, any likely impurity could not affect the course of the reaction, and initial concentrations were always calculated from the OH^- ion concentration in the reaction mixture at the completion of the reaction.

Table I summarizes the results of these experiments for all except glycol diacetate, and this last-named behaves in exactly the same way (rate and activation energy) as glycol monoacetate, when ester concentration is expressed in terms of moles of acetate groups per liter (*cf.* Meyer's equation[3]).

The esters fall into a series: isopropyl, ethyl, 2-ethoxyethanol-1 and glycol acetates with increasing velocity constants

TABLE I

Ester	Velocity constant[a] (mole⁻¹ min.⁻¹ liters) 15°	20°	25°
Isopropyl acetate	0.335	0.49	0.68
Ethyl acetate	1.79	2.53	3.67
2-Ethoxyethanol-1 acetate	3.56	5.75	8.83
Glycol monoacetate	7.37	10.52	14.12

[a] Estimated error ±1%.

However, when activation energies are considered, a discrepancy shows up (see Fig. 1). In all cases but one, the energy of activation is 11,700 ± 300 cal./mole but 2-ethoxyethanol-1 acetate (ethyl cellosolve acetate) gives a value of 15,400 ± 300 cal./mole.

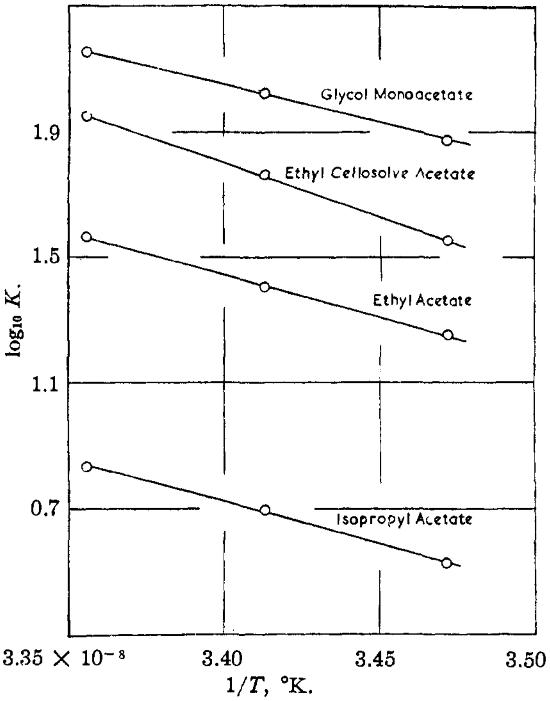

Fig. 1.—Activation energies of series of esters.

Discussion.—The increasing velocity constants of alkaline hydrolysis in this series of esters is to be expected on account of the increasing basic strength; $(CH_3)_2CH-$, C_2H_5-, $C_2H_5OC_2H_4-$ and HOC_2H_4-. At the same time, for a reaction in solution between a dipolar molecule and an ion, a constant value for the energy of activation in such a series is not surprising.[4]

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* Harvard University, Eli Lilly Research Fellow, 1948–1949.

(1) From work done at the Department of Colloid Science, University of Cambridge, England.

(2) Rabinovitch and Alexander, THIS JOURNAL, 72, 293 (1950).

(3) J. Meyer, *Z. physik. Chem.*, 67, 257 (1909).

(4) Moelwyn-Hughes, "Kinetics of Reactions in Solution," Oxford University Press, 1947, p. 124.