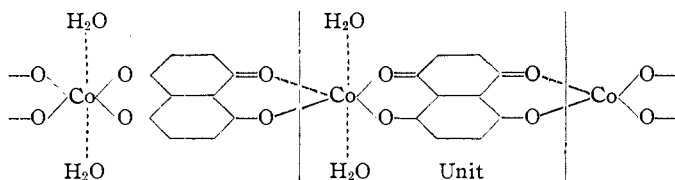


Analysis of tetrahydrate. Calcd.: C, 38.40; H, 4.26; N, 7.47; Co, 15.75. Found: C, 38.45, 38.60; H, 4.01, 3.93; N, 7.84, 7.84; Co, 15.70, 15.84.

When allowed to stand open to air the pink crystals slowly absorbed water and changed from pink back to yellow-orange. They would not absorb oxygen.

7. **Cobalt Di-(*o*-aminobenzal)-ethylenediimine.**—The Schiff base was prepared by mixing *o*-aminobenzaldehyde and ethylenediimine in a mixture of ethanol and dioxane. To this hot solution of Schiff base was added a hot aqueous solution of cobaltous acetate. A nicely crystallized red product was formed which was unsolvated. All efforts to solvate it with pyridine, etc., were in vain. The compound would not take up oxygen. Calcd.: C, 59.45; H, 4.96; N, 17.34; Co, 18.27. Found: C, 59.28, 59.28; H, 4.66, 4.56; N, 17.89, 18.09; Co, 17.8, 17.3.

8. **Cobalt Naphthazarin (Polymer).**—Excess naphthazarin was extracted off with ether.



Anal. Calcd.: C, 42.4; H, 2.83; Co, 20.85. Found: C, 41.5, 41.5; H, 3.00, 3.07; Co, 20.3, 20.2.

When heated a sample lost 10.0% in weight, calcd. for 2H₂O per cobalt is 12.7%. Slowly absorbs water from the air following desolvation.

9. **Cobalt Di-(1-[*o*-hydroxyphenyl]-isoquinoline).**—Precipitates as a monohydrate which is inert to oxygen after removal of the hydrated water.

Analysis of hydrate. Calcd.: C, 69.62; H, 4.26; N, 5.42; Co, 11.42. Found: C, 69.65, 69.78; H, 4.27, 4.32; N, 5.48, 5.53; Co, 11.61, 11.74.

10. **Cobalt Di-(*o*-hydroxyacetophenone)-propylenediimine** was a red crystalline unsolvated compound; inert to high pressure oxygen. Calcd.: C, 62.15; H, 5.45;

N, 7.63; Co, 16.1. Found: C, 62.11, 62.05; H, 5.62, 5.65; N, 7.82, 7.92; Co, 16.1, 16.4.

11. **Cobalt Di-(2-hydroxy-3-ethoxyacetophenone)-ethylenediimine.**—This one exists in two forms, one a red crystalline unsolvated form which is inert to high pressure oxygen. The other form is a yellow material which may be hydrated as a sample lost 8.34% in weight when heated one and one-half hours at 170° *in vacuo*; calcd. for 2H₂O, 7.54%. A sample absorbed 2.04% oxygen when exposed at 125 p.s.i. oxygen pressure for half an hour. Calcd.: C, 59.90; H, 5.90; N, 6.35; Co, 13.38. Found: C, 59.9, 59.7; H, 6.14, 6.19; N, 6.40, 6.54; Co, 13.5, 13.2.

12. **Cobalt Di-(acetylaceton)-ethylenediimine.**—This orange-red compound was prepared according to Morgan.⁹ It would absorb huge quantities of oxygen but most of it was of an irreversible nature. Frequently the chelate compound would burn in oxygen, particularly under high pressures of oxygen.

13. **Cobalt Di-(salicylaldoxime).**—Prepared in aqueous alcohol, and red crystals were formed. They were washed with water, alcohol and ether, then dried in a vacuum desiccator. A sample lost 3.4% in weight when heated to 125° *in vacuo*, and turned black. When exposed to high pressure oxygen the sample increased slightly in weight.

Analysis of red form. Calcd.: C, 50.8; H, 3.63; N, 8.46; Co, 17.83. Found: C, 50.87, 50.93; H, 3.71, 4.01; N, 8.45, 8.62; Co, 17.84, 17.74.

Analysis of black crystals. Found: C, 51.40, 51.47, 51.64; H, 3.39, 3.42, 3.58; N, 8.41, 8.21; Co, 18.01, 18.07, 18.08.

Summary

A group of fifty-seven chelate compounds have been prepared, characterized, and tested for the oxygen carrying properties.

(9) Morgan, *J. Chem. Soc.*, 117, 1457 (1920).

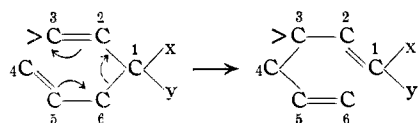
BERKELEY, CALIFORNIA RECEIVED DECEMBER 23, 1946

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF WISCONSIN AND THE CHEMICAL LABORATORY OF BRYN MAWR COLLEGE]

Activation Energies and Entropies of Activation in the Rearrangement of Allyl Groups in Three Carbon Systems¹

BY E. GORDON FOSTER,² ARTHUR C. COPE³ AND FARRINGTON DANIELS

The rearrangement of allyl groups in three-carbon systems was first reported by Cope and Hardy.⁴ The general reaction reported was as follows



where x and y are CN or COOC₂H₅ groups.

The belief was expressed that the reaction was

(1) An abstract of a thesis presented by E. G. Foster to the faculty of the University of Wisconsin as partial fulfillment for the requirements of the Master of Science degree, June, 1942.

(2) Present address: E. I. du Pont de Nemours & Co., Wilmington, Del.

(3) Present address: Massachusetts Institute of Technology, Cambridge, Massachusetts.

(4) Cope and Hardy, *THIS JOURNAL*, **62**, 441 (1940).

analogous to the Claisen rearrangement and occurred by the same cyclic mechanism.^{4,5} According to this mechanism, the number 4 carbon atom approaches the number 3 carbon atom and simultaneously electron pairs shift from the 1-6 position to the 1-2 position, from the 4-5 position to the 5-6 position, and from the 2-3 position to the 3-4 position. This cyclic mechanism was substantially confirmed when it was shown that the reaction was intramolecular and proceeded with an inversion of methyl substituted allyl groups.⁶

In a series of kinetic studies⁷ it was demonstrated that the reaction was first order. It was also shown that the more electronegative the

(5) Hurd and Pollack, *J. Org. Chem.*, **3**, 550 (1939).

(6) Cope, Hofmann and Hardy, *THIS JOURNAL*, **63**, 1852 (1941).

(7) Cope, Hoyle and Heyl, *ibid.*, **63**, 1843 (1941).

groups x and y, the faster the reaction rate. That is, the rate of reaction was increased when a COOC_2H_5 group was replaced by a CN group. Thus the decreasing rate of rearrangement was in the order malonitriles > cyanoacetic esters > malonic esters.

It has been subsequently reported that the rearrangement readily proceeds to completion when a single nitrile, carboxyl or phenyl group is at-

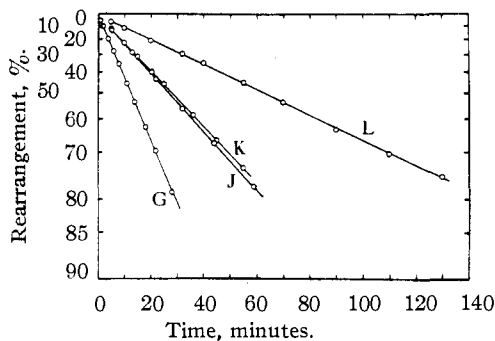


Fig. 1.—Rate of rearrangement of 1-cyclohexenyl allylmalonitrile: G, t is $140.00 \pm 0.1^\circ$, k is $9.14 \times 10^{-4} \text{ sec.}^{-1}$; J, t is $130.56 \pm 0.1^\circ$, k is $4.22 \times 10^{-4} \text{ sec.}^{-1}$; K, t is $130.00 \pm 0.1^\circ$, k is $4.09 \times 10^{-4} \text{ sec.}^{-1}$; L, t is $120.00 \pm 0.1^\circ$, k is $1.806 \times 10^{-4} \text{ sec.}^{-1}$.

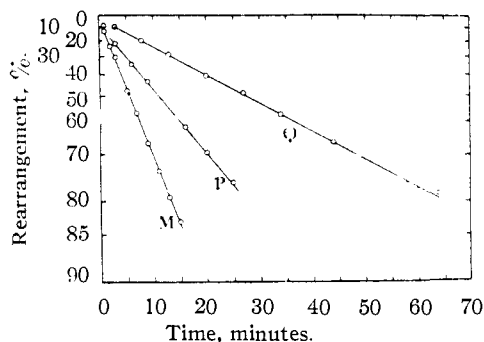


Fig. 2.—Rate of rearrangement of 1-ethyl propenyl allylmalonitrile: M, t is $139.97 \pm 0.1^\circ$, k is $19.83 \times 10^{-4} \text{ sec.}^{-1}$; P, t is $129.96 \pm 0.1^\circ$, k is $9.12 \times 10^{-4} \text{ sec.}^{-1}$; Q, t is $120.03 \pm 0.1^\circ$, k is $4.02 \times 10^{-4} \text{ sec.}^{-1}$.

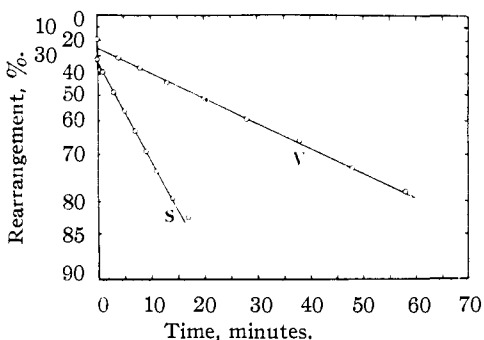
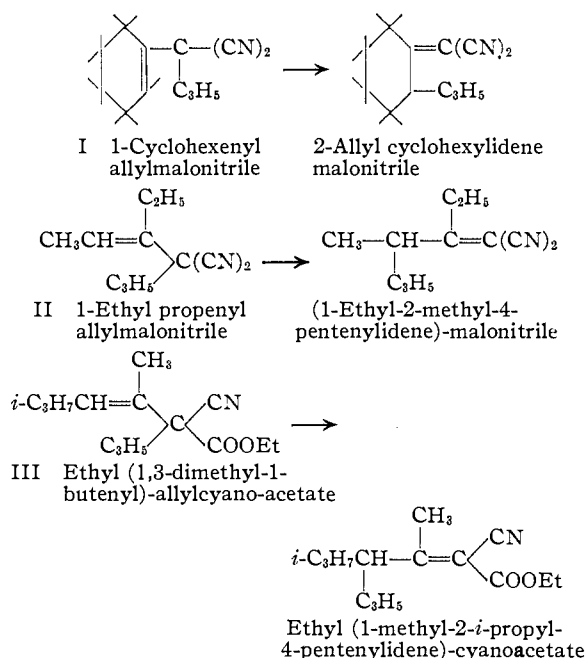


Fig. 3.—Rate of rearrangement of ethyl (1,3-dimethyl-1-butenyl)-allylcyanoacetate: S, t is $200.39 \pm 0.1^\circ$, k is $14.00 \times 10^{-4} \text{ sec.}^{-1}$; V, t is $179.92 \pm 0.1^\circ$, k is $3.54 \times 10^{-4} \text{ sec.}^{-1}$.

tached to the alpha carbon atom,^{8,9} and it has been further shown that the rearrangement proceeds when a methyl group is attached to the alpha carbon atom, but only at a much higher temperature and not to completion.⁹

Electron attracting groups at x and y are believed to increase the rate of reaction by their attraction for the electron pair between carbon atoms 1 and 6 which in turn lowers the dissociation energy at this bond.^{4,7}

The purpose of the study reported here has been to measure the reaction rate of three of the rearrangements at different temperatures to permit a calculation of the energies and entropies of activation. Previous kinetic measurements⁷ of each rearrangement were made only at a single temperature. The rearrangements which were studied are



Results

The experimental results are summarized in Figs. 1, 2 and 3 in which the logarithm of the per cent. of unrearranged reactant is plotted against the time in minutes. The first order reaction rate

Reactant	Temp., °C.	k , sec. ⁻¹ $\times 10^4$
I	120.00 ± 0.1	1.806
	$130.00 \pm .1$	4.09
	$130.56 \pm .1$	4.22
	$140.00 \pm .1$	9.14
II	$120.03 \pm .1$	4.02
	$129.96 \pm .1$	9.12
	$139.97 \pm .1$	19.83
III	$179.92 \pm .1$	3.54
	$200.39 \pm .1$	14.00

(8) Whyte and Cope, *THIS JOURNAL*, **65**, 1999 (1943).

(9) Levy and Cope, *ibid.*, **66**, 1684 (1944).

TABLE II

Reactant	$s \times 10^{-10}$	E	$T, ^\circ\text{K.}$	ΔS^\ddagger	$T\Delta S^\ddagger$	Incremental $T\Delta S^\ddagger$	Inc. E	$\frac{100 \text{ Inc. } E}{\text{Inc. } T\Delta S^\ddagger + \text{Inc. } E}, \%$
I, 1-Cyclohexenyl allyl malonitrile	6.31	26,160	403	-11.7	4720			
Increment II-I						-250	-380	60.3
II, 1-Ethyl propenyl allyl malonitrile	8.66	25,780	403	-11.1	4470			
Increment III-II						2010	2840	58.6
III, Ethyl (1,3-dimethyl-1-butenyl) allylcianoacetate	2.28	28,620	463	-14.0	6480			
Increment III-I						1760	2460	58.2

constants have been calculated from these graphs according to the equation $k = -(2.303/60) \times \text{slope}$, where the slope is that of the corresponding graph. The reaction rate constants are summarized in Table I.

The above results have been fitted to the equation

$$k = se^{-E/RT}$$

with the help of Fig. 4 in which $\log k$ is plotted against $1/T$. The energies of activation have been calculated from these plots by the equation $E = -2.303R \times \text{slope}$, where $R = 1.987$ calories per degree, and the slope is that of the corresponding plot of $\log k$ versus $1/T$. The energies of activation (E) and frequency factor (s) are summarized in the third and second columns of Table II.

According to the theory of absolute reaction rates¹⁰

$$k = \frac{k' T e^{\Delta S^\ddagger/R} e^{-\Delta H^\ddagger/RT}}{h} = \frac{k' T e^{\Delta S^\ddagger/R} e^{-E/RT}}{h}$$

where k = first order reaction rate constant

k' = Boltzmann constant = 1.3805×10^{-16} erg/ $^\circ\text{K.}$

T = absolute temperature, $^\circ\text{K.}$ ($273.15 + ^\circ\text{C.}$)

h = Planck constant = 6.624×10^{-27} erg sec.

ΔS^\ddagger = difference in entropy between initial and activated states in entropy units

ΔH^\ddagger = difference in internal energy between initial and activated states in calories per mole.

E = experimental activation energies, calories

= $-R \frac{d \ln k/d}{d(1/T)}$

$R = 1.987$ cal./ $^\circ\text{K.}$

If we determine s by fitting the equation $k = se^{-E/RT}$ to the experimental data, and set s equal to $k'T/h e^{\Delta S^\ddagger/R}$, and solve for ΔS^\ddagger , we get

$$\Delta S^\ddagger = R \ln s - R \ln (k'T/h)$$

The values of the entropies of activation, ΔS^\ddagger , calculated by this equation are tabulated in the fifth column of Table II, and the temperature values used in the equation are tabulated in the fourth column. These temperatures are the mean temperatures for each series of experiments.

In order to determine which portion of the difference in rearrangement rates of the three compounds was due to differences in energies of activation, and which portion was due to differences in entropies of activation, incremental values of $T\Delta S^\ddagger$ and E have been calculated and are given in the seventh and eighth columns of Table II.

(10) Eyring, *J. Chem. Phys.*, **3**, 107 (1935); Wynne-Jones and Eyring, *ibid.*, 492 (1935); Glasstone, Laidler, and Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941

In the last column is given the per cent. of the differences in reaction rate that can be attributed to differences in energies of activation. From the values in this column it can be seen that approximately 60% of the differences in rearrangement rates is due to differences in energies of activation and the other 40% to differences in entropies of activation.

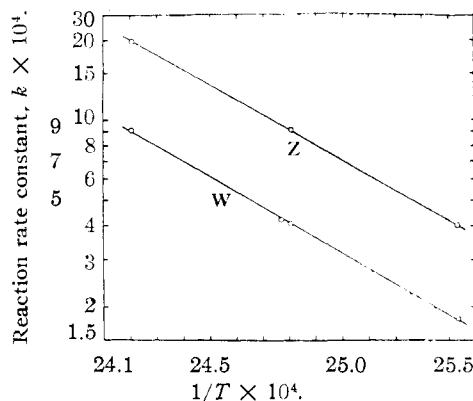


Fig. 4.—Rate of rearrangement of: W, 1-cyclohexenyl allylmalonitrile; Z, 1-ethylpropenyl allylmalonitrile.

The large decrease in entropy in the activation for these rearrangements indicates that several degrees of freedom may be restricted in the activated complex as would be expected for the formation of an activated molecule which involves the formation of a cyclic structure with the corresponding tendency to restrict the motion of some of the atoms.

Experimental¹¹

The rate of reaction was followed by the change in refractive index as previously described.⁷ Pyrex tubing (6 mm. o. d.) was cut into 8-cm. lengths and soaked in a solution of potassium dichromate in sulfuric acid, thoroughly rinsed and dried. The tubes were then sealed at one end and a few drops of the liquid compound inserted. The contents were then frozen with a Dry Ice-bath and the tube evacuated to a pressure of 1 mm. or less and sealed. A glass hook was formed at the end to facilitate handling. About ten of these samples were attached to wires and simultaneously inserted in an oil-bath thermostatically regulated to $\pm 0.05^\circ$. The temperature of the bath was measured with totally immersed thermometers graduated in tenths of a degree and calibrated by the Bureau of Standards. In the case of the measurements with ethyl (1,3-dimethyl-1-butenyl)-allylcianoacetate it was necessary to apply a small stem correction because of the position of the scale on the thermometer used.

(11) We are indebted to Miss Dorothea Heyl for preparation of pure samples of I, II and III.

At successive intervals of time samples were quickly removed and plunged into ice water to arrest the reaction. The refractive index was determined at $25.00 \pm 0.01^\circ$ with an Abbé refractometer with an estimated accuracy of ± 0.0001 . The refractometer was calibrated with a test-plate prior to each series of readings.

The above procedure gave satisfactory results for the rate measurements with 1-cyclohexenyl allylmalonitrile. For the rate measurements with 1-ethylpropenyl allylmalonitrile, however, somewhat erratic results were obtained and the end-product had a refractive index different from that of the desired pure product. It was suspected that a side reaction was occurring at the glass surface. Accordingly, the interior of each sample tube was flamed with a gas flame to poison any catalytic surface prior to the introduction of any compound. This procedure gave satisfactory results and was thereafter used for measuring the rates of rearrangement of both 1-ethylpropenyl allylmalonitrile and ethyl (1,3-dimethyl-1-butenyl)-allylcianoacetate.

The per cent. rearrangement for any given time was calculated by the equation

$$\% \text{ rearrangement} = 100 (n - n_{\text{reactant}}) / (n_{\text{product}} - n_{\text{reactant}})$$

where $n = n_{\text{D}} =$ refractive index of reaction mixture at

any given time, $n_{\text{reactant}} =$ refractive index of pure reactant, and $n_{\text{product}} =$ refractive index of pure product.

Summary

1. The energies and entropies of activation have been determined for the rearrangement of the allyl groups of 1-cyclohexenyl allylmalonitrile, 1-ethylpropenyl allylmalonitrile, and ethyl (1,3-dimethyl-1-butenyl)-allylcianoacetate. The entropies of activation are, respectively, -11.7 , -11.1 and -14.0 e.u. These high entropies of activation substantiate the cyclic mechanism previously advanced.

2. Approximately 60% of the differences in rearrangement rates of the series of compounds studied could be attributed to differences in energies of activation. The other 40% was due to differences in entropies of activation.

MADISON, WIS.

RECEIVED MARCH 18, 1947

[CONTRIBUTION FROM THE SOUTHERN REGIONAL RESEARCH LABORATORY¹]

A Calorimetric Investigation of Moisture in Textile Fibers^{1a}

BY FRANK C. MAGNE, H. J. PORTAS AND HELMUT WAKEHAM

The heat of fusion, or calorimetric, method for the evaluation of bound water has been applied to a wide variety of plant and animal materials with varying degrees of success in attempts to elucidate the nature of water in such substances.²⁻⁷ Certain difficulties encountered in experimental application of the method and in interpretation of the results have led in some cases to the obvious conclusion that the method may be applied only to systems in which all the "free" water will freeze.^{2,8}

In the present investigation the calorimetric method has been applied to cellulose, nylon and glass fibers.

Modern concepts of the mechanism of moisture adsorption by cellulose fibers involve three steps⁹⁻²³: (a) the selective adsorption of water

molecules by hydrogen bonding to the free hydroxyl groups in the noncrystalline or intermicellar regions; (b) the adsorption of water into the lattice of the crystalline regions in those particular cellulose structures exhibiting changes in cellular dimensions with moisture adsorption, such as regenerated or mercerized cellulose fibers; and (c) capillary condensation or "multiple-layer formation" in those spaces in the cellulose fiber which permit occupancy by additional water molecules.

Of these three classifications, the water adsorbed in the first two may be considered as "bound" with energies greater than those involved in the water-to-water hydrogen bond. Conversely the water taken up by capillary condensation might be expected to behave similarly to bulk water and to freeze under suitable conditions.

The experimental demonstration of this hypo-

(1) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

(1a) Presented before the Division of Cellulose Chemistry at the 110th meeting of the American Chemical Society, Chicago, Illinois, September 9 to 13, 1946.

(2) A. J. Stamm, "Colloid Chemistry of Cellulosic Materials," U. S. Dept. of Agriculture, Misc. Pub. No. 240, 1936, p. 48.

(3) R. A. Gortner, "Outlines of Biochemistry," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1938, p. 285.

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(22) A. J. Stamm and M. A. Millett, *J. Phys. Chem.*, **45**, 43 (1941).

(23) A. R. Urquhart, *J. Textile Inst.*, **20**, 125T (1929).