

taining less fluorine and more chlorine. All of the silicon halides decompose readily in moist air or ammonia and could account for all the results shown in Table I. In the earlier experiments no tests were made for the presence or absence of fluoride ion in the hydrolyzed products since it has been assumed that the carbon-fluorine bond was too stable to be ruptured by conditions of the reaction being studied. However, after the distillation results were available attention was turned to tests for both chloride and fluoride ions in the hydrolyzed products.

Detailed results of these experiments are shown in Table II. The primary purpose of these experiments was to col-

TABLE II

Silicon form	Reagent	Temp., °C.	Ratio F <sup>-</sup> /Cl <sup>-</sup>	Remarks
Metal	CF <sub>3</sub> Cl	1000	3/1	Vigorous reactn.
Metal	C <sub>2</sub> F <sub>6</sub> Cl	1000	ca. 5/1	Vigorous reactn.
Metal	CF <sub>3</sub> Cl	800	3/1	Exothermic
Metal	CF <sub>3</sub> Cl	500	3/1	Slow reactn.

lect the reaction products in a form that could be analyzed for both fluoride and chloride ions. The reaction products were collected in Dry-Ice cooled methanol in one trap backed up with an aqueous caustic trap. At the conclusion of the run the contents of the two traps were mixed and the products analyzed for the ratio of fluoride ion to chloride ion. The analyses suggest that instead of the expected addition reaction both chlorine and fluorine were being stripped from the carbon by the silicon and that the silicon halides were being hydrolyzed completely to liberate all halogen in ionic form.

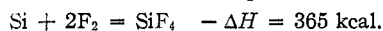
Numerous other runs were made at various temperatures from 500–1000° to determine whether it might be possible that both addition and halogen transfer were taking place in the low temperature reaction. However, analysis of the product always showed approximately 3 moles fluorine to one mole chlorine and no product suggestive of a silicone intermediate was ever isolated.

A sample, taken from the very center of a well-used silicon bed, was burned in the muffle furnace and 90% of the material oxidized away, indicating it to be carbon. In a

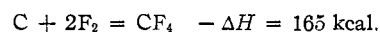
similar experiment using pure silicon there was a gain in weight in the muffle furnace and some of the silicon was converted to silica.

It was observed at these high temperatures that with everything at a steady state an increase in flow of Freon 13 would cause a substantial increase in the temperature recorded by the thermocouple without any change in power input, indicating the reaction to be quite exothermic.

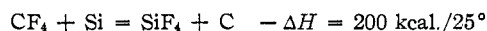
Data available in the literature show that the reaction  $CF_3Cl + Si = C + SiF_3Cl$ , would be highly exothermic. For example for the reaction



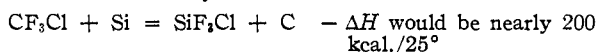
and for the reaction



Therefore for the reaction



and for the closely related reaction



These results demonstrate the impossibility of producing a trifluoromethylsilicon halide by direct reaction of silicon and trifluoromethyl chloride. Although the experiments were not sufficiently quantitative to show conclusively that the exchange of halogen goes to completion, the ease with which this exchange takes place and its exothermic nature make it appear quite probable that the reaction could be readily developed into an analytical method for fluorine and chlorine in volatile perfluorocarbons.

BUFFALO, N. Y.

RECEIVED SEPTEMBER 25, 1950

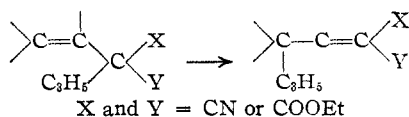
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

## Kinetics of the Rearrangement of Ethyl Isopropenyl Allylmalonate<sup>1a</sup>

BY GERALD R. ALDRIDGE<sup>1b</sup> AND GEORGE W. MURPHY

The kinetics of the rearrangement of ethyl isopropenyl allylmalonate has been studied in the liquid phase over the temperature range 145–200°. The reaction is first order and proceeds to virtual completion. The heat and entropy of activation, 28,400 cal./mole and -13.5 e.u., respectively, lie close to the values reported by Foster, Cope and Daniels for similar rearrangements. The entropy of activation is somewhat lower than expected, and is interpreted in terms of steric factors.

Cope, Hoyle and Heyl<sup>2</sup> have shown that the rearrangement



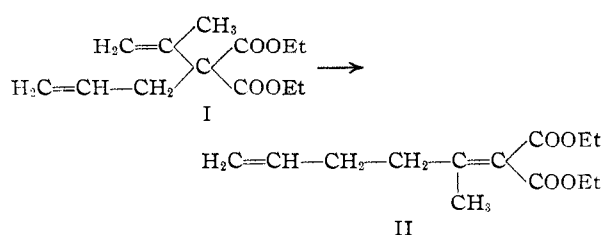
is a general one and have suggested that the mechanism is the same for all compounds having the essential skeleton structure. The most likely mechanism was thought to involve a cyclic intermediate, and this hypothesis received support from the kinetics evidence of Foster, Cope and Daniels<sup>3</sup> on three rearrangements.

(1) (a) An abstract of a thesis presented by Gerald E. Aldridge to the faculty of the University of Wisconsin in partial fulfillment of the requirements for Master of Science, 1950. (b) American Cyanamid Co., Stamford, Conn.

(2) Cope, Hoyle and Heyl, *THIS JOURNAL*, **63**, 1843 (1941).

(3) Foster, Cope and Daniels, *ibid.*, **69**, 1893 (1947).

Cope, Hofmann and Hardy<sup>4</sup> have shown that the rearrangement



proceeds somewhat below the temperature 200°. This rearrangement appeared to the present authors to be a logical one to investigate further by the kinetics approach, since Foster, Cope and Daniels' work did not include a compound where both X and Y were -COOEt groups.

(4) Cope, Hofmann and Hardy, *ibid.*, **63**, 1852 (1941).

### Experimental

**Ethyl Isopropenyl Allyl Malonate (I).**—This compound was prepared according to the directions of Cope and Hancock.<sup>5</sup> Condensation of 976 g. (6.1 moles) of ethyl malonate with acetone yielded 590 g. (48.5%) of ethyl isopropylidene malonate. The recovery of ethyl malonate was 386 g. (39.5%). Alkylation of 100 g. (0.5 mole) of ethyl isopropylidene malonate with allyl bromide yielded 81.7 g. (68.1%) of I, b.p. 122–123° (10 mm.),  $n_D^{25}$  1.4500.

**Ethyl (1-Methyl-4-pentenylidene) Malonate (II).**—For the preparation of this compound, Cope, Hofmann and Hardy<sup>4</sup> heated I for 14 hours, at 180–190°. Our kinetics studies at various temperatures indicated that virtually complete rearrangement should occur in a much shorter time. Our best product was obtained by allowing I to rearrange for 135 minutes at a temperature of 178°. After adding a little hydroquinone to inhibit polymerization, the material was vacuum-fractionated in a Pirox-Glover Micro Still, having about 20 theoretical plates when operated under vacuum. Changing refractive index and carbon-hydrogen analyses had<sup>4</sup> indicated strong oxygen absorption when this compound was allowed to stand in air. For this reason, the fractions were quickly transferred to bottles in which the oxygen had been replaced by nitrogen.

From approximately 17 g. of starting material 11 g. (65%) of product was obtained having the following physical constants,<sup>6</sup> b.p. 142–144° (10 mm.),  $n_D^{25}$  1.4607.

*Anal.* Calcd. for  $C_{13}H_{20}O_4$ : C, 64.96; H, 8.39. Found: C, 64.75; H, 8.29.

Some additional product could have been obtained by continued distillation.

**Procedure Employed in Kinetics Investigation.**—The technique of Foster, Cope and Daniels<sup>8</sup> was adapted to this problem. Samples of the starting material were allowed to rearrange in an aluminum block thermostat similar to that described by Hood and Murphy.<sup>7</sup> A mercury thermoregulator in conjunction with an electronic relay maintained the temperature to within  $\pm 0.10^\circ$ . The temperature of the block was measured by means of a thermocouple previously calibrated against a certified platinum resistance thermometer, the thermocouple voltage being read on a Rubicon Portable Precision Potentiometer.

Pyrex tubing (6 mm. o.d.) was cut into 18-cm. lengths and sealed at one end. Approximately 8 cm. from the sealed end each tube was drawn out into a capillary. The exterior of each sample tube was heated with a gas flame to poison any catalytic surface prior to the introduction of the compound. By means of a long pipet approximately six drops of the liquid compound was inserted.

The contents were frozen with a Dry Ice-acetone-bath and the tube evacuated to a pressure of about 1 mm. and sealed. In each run 10 or 11 of these tubes were inserted in the block and the time of each insertion noted. A little Wood's metal at the bottom of the block ensured good thermal contact. After certain definite time intervals the tubes were quickly removed and plunged into ice-water. The refractive index was determined at  $25.00 \pm 0.02^\circ$  with a Valentine precision refractometer with an estimated precision of  $\pm 0.0001$ .

Before each run the approximate time for the rearrangement to be 99.5% complete at the temperature of the run was calculated. In each run one tube was left in the block for a period of time longer than that required for 99.5% rearrangement. The refractive index of the material in this tube was substituted for the  $n_p$  in the formula used to calculate the per cent. unrearranged.

### Experimental Results

The rate of the reaction was followed by measuring the refractive index at different time intervals. The per cent. unrearranged was calculated from the formula

$$\% \text{ unrearranged} = \frac{100(n_p - n_t)}{n_p - n_r}$$

where  $n_p$  = the refractive index of the pure

(5) Cope and Hancock, *THIS JOURNAL*, **60**, 2645 (1938).

(6) Cope, Hofmann and Hardy<sup>4</sup> published b.p. and  $n_D^{25}$  of pure product as 134–136° (10 mm.) and 1.4610, respectively.

(7) Hood and Murphy, *J. Chem. Education*, **26**, 169 (1949).

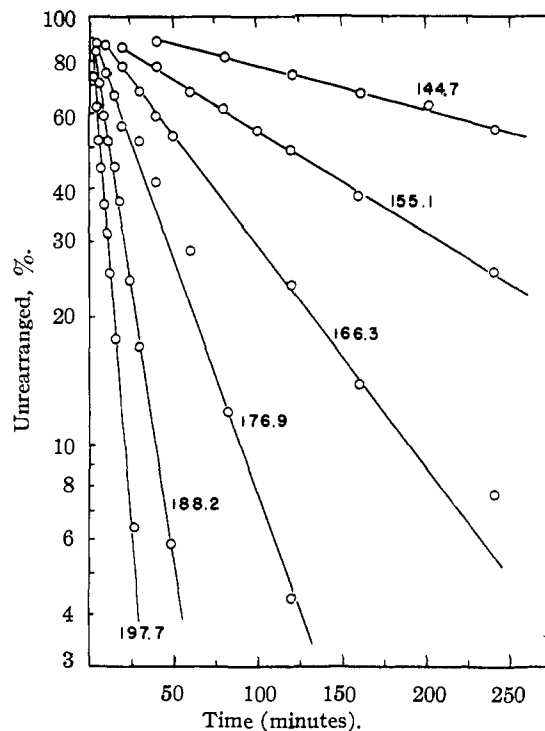


Fig. 1.—Rearrangement data plotted according to first order rate equation; temperatures in degree centigrade.

product,  $n_t$  = refractive index of reaction mixture at any given time, and  $n_r$  = refractive index of pure reactant. Linearity of the refractive index-composition curve was verified experimentally. The reaction is first order, as evidenced by the straight line plots of  $\log (\% \text{ unrearranged})$  vs. time (Fig. 1). The specific rate constants have been calculated from the slopes of these lines, and are listed in Table I.

TABLE I

SPECIFIC RATE CONSTANTS FOR THE REARRANGEMENT OF ETHYL ISOPROPENYL ALLYLMALONATE

Temp., °C.	$k(\text{sec.}^{-1}) \times 10^6$
197.7	188
188.2	98.7
176.9	43.0
166.3	20.0
155.1	9.52
144.7	4.03

In Fig. 2  $\log k$  has been plotted against  $1/T$ . The points are seen to fall on a straight line. The data are represented by the equation

$$k = 2.83 \times 10^{10} \exp. (-28,400/RT) \text{ sec.}^{-1}$$

This equation was compared with that of Eyring for unimolecular reactions<sup>8</sup>

$$k = \kappa e(k'T/h) \exp. (\Delta S^\ddagger/R) \exp. (-\Delta E/RT)$$

where  $\kappa$  is the transmission coefficient,  $k'$  is Boltzmann constant,  $\Delta S^\ddagger$  is the entropy of activation,  $\Delta E = RT^2(d \ln k)/dT$  is the experimental energy of activation, and the other symbols have their usual significance. The average value of the entropy of activation over the temperature range

(8) Glasstone, Laidler and Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, 1941, p. 199.

studied was found to be 13.5 e. u., making the usual assumption that the transmission coefficient is unity.

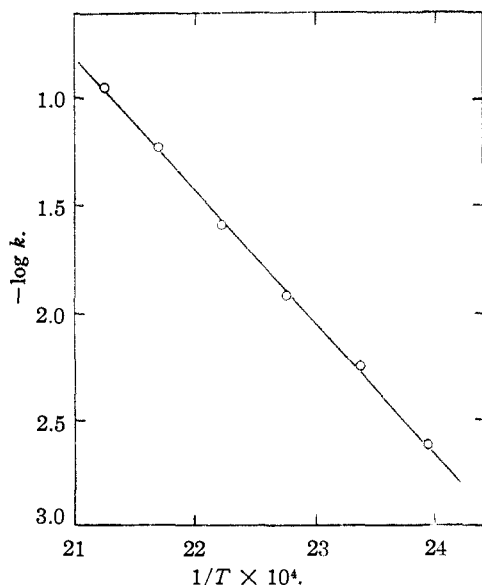


Fig. 2.—Dependence of rate constants of Table I on temperature.

### Discussion

The values of  $s$ ,  $\Delta E$  and  $\Delta S^\ddagger$  are presented in Table II along with similar values for the three compounds studied by Foster, Cope and Daniels.

In all of these reactions the large decrease in entropy accompanying the activation process is an indication that the rearrangement proceeds by way of a cyclic mechanism, inasmuch as a cyclic intermediate would have fewer degrees of rotational freedom than the reactant molecule.

Cope, Hoyle and Heyl<sup>2</sup> observed that the decreasing the rate of rearrangement was in the order malononitriles > cyanoacetic esters > malonic esters. A study of Table II reveals that both the cyanoacetate and malonic ester have higher heats and more negative entropies of activation, and therefore lower rate constants at a given temperature than the malonitrile. Our data

TABLE II  
COMPARISON OF CONSTANTS IN THE ARRHENIUS AND EYRING EQUATIONS FOR FOUR REARRANGEMENTS

Reactant	$s$ (sec. <sup>-1</sup> ) $\times 10^{-10}$	$\Delta E$ (cal./mole)	$\Delta S^\ddagger$ (entropy units)
Foster, Cope and Daniels			
1-Cyclohexenyl allylmalononitrile	6.31	26,160	-11.7
1-Ethyl propenyl allylmalononitrile	8.66	25,780	-11.1
Ethyl-(1,3-dimethyl-1-butenyl (allylcianoacetate	2.28	28,620	-14.0
This paper			
Ethyl isopropenyl allylmalonate	2.82	28,400	-13.5

show that the malonic ester, however, has about the same heat and entropy of activation as the cyanoacetate.

Cope, Hoyle and Heyl did, however, allow for the possibility of other structural features affecting the rate of rearrangement, particularly steric factors. We have constructed Fisher-Hirschfelder models of a malononitrile similar to the malonic ester. Rotation of the allyl group with respect to the isopropenyl group, which brings about the orientation favorable to rearrangement, was found to be virtually unhindered by the two cyano groups. When one of the cyano groups was replaced by a carboethoxy group the rotation of the allyl group was hindered to an appreciable extent by the carboethoxy group. In the case where both cyano groups were replaced by carboethoxy groups the hindrance to the motion of the allyl group did not appear to be noticeably greater than the hindrance observed when only one carboethoxy group was present. On the basis of the above observations the similarity in the entropies of activation for the cyanoacetate and malonic ester can be explained.

The authors have been assisted by discussion with Professors Farrington Daniels and A. L. Wilds, and by correspondence with Professor A. C. Cope.

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