

with a small amount of cold benzene. The precipitate formed was filtered off, and, after another benzene treatment, 2.16 g. of benzalmalonic acid, m. p. 187–192° (with decomposition), was obtained.²¹ This compound was not further purified because of its high solubility in water and its tendency to decompose.

The benzene solutions were evaporated, the oily residue treated with dilute sodium carbonate and the alkaline solution extracted with ether. The alkaline solution yielded 0.5 g. of cinnamic acid, m. p. 130–132°, on acidification and subsequent recrystallization of the precipitate from hot water. The total yield of ethyl benzalmalonate, based on both the crude benzalmalonic and cinnamic acids, was 3.6 g. (9.7% of calcd.). It is probable that more ethyl benzalmalonate was formed in the reaction but was decomposed to benzaldehyde and malonic acid during the hydrolysis.²¹

This experiment was repeated several times under varying conditions, and in every case some condensation apparently occurred, although it was not always possible to isolate the products. In addition to ethyl benzalmalonate, a high-boiling oil generally was obtained in considerable amount. This was presumably a Michael condensation product, formed by the reaction of unchanged sodium ethyl malonate with ethyl benzalmalonate. In every case considerable amounts of Cannizzaro reaction prod-

(21) Claisen and Crismer [*Ann.*, **218**, 136 (1883)] give 195–196° as the melting point of this compound.

ucts, benzyl alcohol and benzoic acid, were obtained, as previously reported by Müller and co-workers.⁷

Summary

1. Contrary to the result of other workers, we have confirmed Fittig's original result with benzaldehyde, isobutyric anhydride and sodium isobutyrate, in which the isobutyryl derivative of the "aldol" is formed.

2. Ethyl isobutyrate (as enolate) has been condensed with benzaldehyde by means of sodium triphenylmethyl to form ethyl phenylhydroxy-pivalate.

3. The condensation of ethyl acetate with benzaldehyde, brought about by sodium triphenylmethyl, has been arrested at the "aldol" stage, and ethyl phenylhydroxypropionate isolated from the reaction mixture.

4. It has been found that the sodium enolate of ethyl malonate condenses with benzaldehyde in the presence of a proton donor.

5. The mechanism of the Perkin type of condensation is discussed.

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The Theory of Absolute Reaction Rates and the Polymerization of Ethylene

BY FRANCIS P. JAHN

It is well known that the simple collision theory of reaction kinetics is not in accord with the rate of the homogeneous thermal polymerization of ethylene.¹ Pease¹ has shown that the rate calculated from the collision number and the experimental energy of activation is about two thousand times greater than the experimental rate. Rice and Gershinowitz² have accounted for the rates of this and three other well-known bimolecular association reactions by a method which is essentially the same in principle as that used in this paper. It seemed worth while, however, to emphasize by a set of calculations that the rate of the ethylene polymerization may be satisfactorily predicted over the experimental temperature range by means of the somewhat more straightforward assumptions of the theory of absolute reaction rates as set forth by Eyring.³ Wynne-Jones and Eyring⁴ have used the same

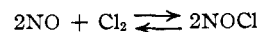
method in calculating a steric factor of 10^{-6} for the formation of cyclopentane and methyl radical from *n*-hexyl radical, thus justifying the assignment of F. O. Rice.

The expression for the rate constant of a reaction is, in the thermodynamic form⁴

$$K = \kappa \frac{kT}{h} e^{\Delta S^*/R} e^{-\Delta H^*/RT} \quad (1)$$

where κ is the transmission coefficient and ΔS^* and ΔH^* are, respectively, the entropy and heat of activation.

Welinsky and Taylor in a study of the rates of the nitric oxide-chlorine combination and the nitrosyl chloride decomposition have shown that the difference between the entropies of activation of the forward and reverse reactions at a given temperature is equal to the standard entropy increase for the equilibrium



when this entropy increase is evaluated for the standard state corresponding to the concentration

(1) Pease, *THIS JOURNAL*, **53**, 613 (1931).

(2) O. K. Rice and Gershinowitz, *J. Chem. Phys.*, **2**, 853 (1934).

(3) Eyring, *ibid.*, **3**, 107 (1935).

(4) Wynne-Jones and Eyring, *ibid.*, **3**, 492 (1935).

TABLE I
 CALCULATION OF THE RATE OF ETHYLENE POLYMERIZATION

$T, ^\circ\text{K.}$	$-\Delta S^*$ cal./deg.	ΔH^* cal.	$kT/h \times 10^{-13}$ sec. ⁻¹	$e^{-\Delta H^*/RT}$ $\times 10^{12}$	$e^{\Delta S^*/R}$ $\times 10^3$	$3600 \times 2 \times K_1$ atm. ⁻¹ hr. ⁻¹	$K_{\text{obsd.}}$	$K_{\text{calcd.}}/K_{\text{obsd}}$
623	34.50	33,030	1.305	2.578	2.885	0.0070	0.0056	1.25
648	34.73	32,880	1.357	8.112	2.565	.0203	.0165	1.23
673	35.00	32,730	1.407	23.44	2.291	.0545	.0374	1.45
698	35.17	32,580	1.462	62.76	2.052	.1356	.108	1.25
723	35.38	32,430	1.514	156.9	1.846	.316	.243	1.30
748	35.59	32,280	1.566	369.2	1.667	.694	.57	1.22
773	35.78	32,130	1.618	821.8	1.511	1.45	1.3	1.11

units in terms of which the velocity constants are given.⁵

The approximation made in this paper is, explicitly, that in cases in which the reverse reaction is a simple unimolecular decomposition, the entropy of activation for the forward bimolecular association may be taken as sensibly equal to the standard entropy increase for the reaction. This assumption has been discussed by Rice and Gershinowitz² and by Kistiakowsky and Lacher.⁶

It would seem likely that in this case the activated complex would be approximately linear. The data of Pease¹ show that the primary product of the association is a butylene. Butene-1 will be adopted as giving the approximate configuration of the activated complex. Now the entropy of the complex would differ appreciably from that of butene-1 only in the vibrational contribution; that is to say, the fundamental vibrations of the complex would in general have smaller frequencies than those of butene-1. This of course corresponds to a small entropy of activation for the reverse decomposition, which is here disregarded. The error entailed is at least mitigated by ignoring the vibrational contributions to the heat capacities of both ethylene and butene-1, in evaluating the entropies of activation at higher temperatures from the standard entropy increase at 25°.

From the tables of Pitzer⁷ one finds that the entropy increase for the formation of butene-1 from two moles of ethylene is -30.1 cal./deg. (The standard state is the ideal gas at one atmosphere and 25°.) Taking into account only translations and external and (free) internal rotations, ΔC_p is equal to $-3R$ cal.

The bimolecular velocity constants given by Pease¹ tend to increase with percentage conversion, indicating further reaction with ethylene of the butylene initially formed. The velocity

constants selected for the evaluation of the energy of activation were therefore taken from experiments conducted with small times of contact.

If one substitutes

$$\Delta H^* = \Delta E_0 - 3RT$$

and

$$\Delta S^* = -30.1 - 3R \ln(T/298)$$

in Equation 1, and differentiates with respect to temperature, one obtains (assuming κ independent of temperature)

$$\frac{d \ln K}{dT} = -\frac{2}{T} + \frac{\Delta E_0}{RT^2}$$

or

$$\frac{d \ln(KT^2)}{d(1/T)} = -\Delta E_0/R$$

The value of ΔE_0 obtained by plotting $\log(KT^2)$ against reciprocal temperature is 36,740 cal. The resulting values for ΔH^* , ΔS^* and the values for the velocity constants at each of the temperatures used by Pease obtained by means of Equation 1 are given in the table. The transmission coefficient is taken equal to unity. The values of the velocity constants calculated by Equation 1 actually give the rate of butylene formation per second; they have been multiplied by 3600×2 in column seven to give the constants in hour time-units and in terms of ethylene disappearance. In the eighth and ninth columns appear, respectively, the experimental constants given by Pease¹ and the ratio of calculated to observed constants. The lack of significant trend in the ratios is noteworthy.⁸ The discrepancy is composite of two errors of opposite effect, those involved in taking the transmission coefficient equal to unity and in neglecting the vibrational contribution to the entropy of the complex. It is probable that κ is less than unity.

(8) The lack of trend in the ratios is not critical in so far as the temperature dependence of the entropy and energy of activation is concerned. Thus if one assumes ΔS^* and ΔH^* constant over the experimental temperature range and equal to the values given in Table I for 723°K., the resulting ratios have little more trend than those given in the table. The author is indebted to O. K. Rice for this suggestion.

(5) Welinsky and H. A. Taylor, *J. Chem. Phys.*, **6**, 466 (1938).

(6) Kistiakowsky and Lacher, *THIS JOURNAL*, **58**, 123 (1936).

(7) Pitzer, *J. Chem. Phys.*, **5**, 473 (1937).

The agreement is a justification of the approximations made. Eyring has justly remarked that one has much more *a priori* reason for making the guesses involved in the application of his method, than in the classical collision theory.

It may be well to illustrate by a sample calculation how the units of the calculated velocity constant are determined by the standard state for the entropy of activation. For example, to calculate the velocity constant in liter per mole-second units at 723°K., one must evaluate the standard entropy of activation at such a pressure that each gas concentration is one mole per liter. The entropy of activation for the standard state of one atmosphere and 723°K. is -35.38 cal./deg.

$$n/V = P/RT = 1$$

or

$$P = 0.08207 T \text{ atm.}$$

$$\frac{\partial(\Delta S^*)}{\partial P} = -\frac{\partial(\Delta V^*)}{\partial T} = -\Delta n \frac{\partial(RT/P)}{\partial T} = \frac{R}{P}$$

since $\Delta n = -1$. Then $\Delta S^* = -35.38 + R \ln P = -35.38 + 4.575 \lg(0.08207 \times 723) = -27.27 \text{ cal./deg.}$

$$e^{-27.27/R} = 1.095 \times 10^{-6}$$

Then by Equation 1 K is equal to 5.21×10^{-3} liter-mole⁻¹-sec.⁻¹.

Naturally the operation involved above is equivalent to the ordinary conversion; thus to obtain the constant at 723°K. in liter-mole⁻¹-second⁻¹ units from the calculated constant in atm.⁻¹-sec.⁻¹ units, one divides the latter by the number of moles/liter per atmosphere.

$$K_{723}(\text{liter-mole}^{-1}\text{-sec.}^{-1}) = K_{723}(\text{atm.}^{-1}\text{-hr.}^{-1}) \times \frac{RT}{3600} (\text{atm./mole/l.})$$

$$= \frac{0.316 \times 0.08207 \times 723}{3600} = 5.21 \times 10^{-3} \text{ liter-mole}^{-1}\text{-sec.}^{-1}$$

Summary

1. The rate of the homogeneous thermal polymerization of ethylene has been calculated in satisfactory accord with experiment by means of Eyring's activated complex method, using simple assumptions concerning the entropy of activation.

2. The dependence of the units of the rate constant upon the standard state for the entropy of activation is emphasized.

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The Photolysis of Acetyl Bromide

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The photolysis of acetaldehyde has been studied extensively.¹ Although there is agreement as to the experimental data there has been much controversy over the interpretation of the facts. One theory considers that the step following the absorption of the light is a direct rearrangement into the ultimate products carbon monoxide and methane. Another theory assumes that the photo-activated molecule breaks into free radicals and the final products are formed as a result of secondary reactions involving these radicals. Some of the objections to any interpretation which limits itself to a single type of primary process have been discussed in a previous paper.² In order to secure additional experimental data which would aid in the determination of the nature of the primary processes, it seemed

desirable to study the photolyses of analogous compounds. Acetone, in which the hydrogen in the aldehyde group of acetaldehyde has been replaced by a methyl radical, has been studied repeatedly.³ It appears to yield free radicals somewhat more readily than acetaldehyde but the data suggest that decomposition also occurs by way of a rearrangement mechanism, particularly at the longer wave lengths in the absorption band. In this paper we are presenting data on the photolysis of acetyl bromide which differs from acetaldehyde in that the aldehyde hydrogen has been replaced by a bromine atom.

The literature contains no data on the photochemistry of the acetyl halides but some work has been done on the absorption spectra of the chloride and bromide.⁴ The latter is reported to have

(1) (a) Leighton and Blacet, *THIS JOURNAL*, **55**, 1766 (1933); (b) Leermakers, *ibid.*, **56**, 1537 (1934); (c) Pearson and Purcell, *J. Chem. Soc.*, 1151 (1935); (d) Blacet and Roof, *THIS JOURNAL*, **58**, 278 (1936); (e) Blacet and Volman, *ibid.*, **60**, 1234 (1938).

(2) Rollefson, *J. Phys. Chem.*, **41**, 259 (1937).

(3) (a) Damon and Daniels, *THIS JOURNAL*, **55**, 2363 (1933); (b) Norrish, Crone and Saltmarsh, *J. Chem. Soc.*, 1456 (1934); (c) Leermakers, *THIS JOURNAL*, **56**, 1900 (1934); (d) Spence and Wild, *J. Chem. Soc.*, 352 (1937); (e) Matheson and Noyes, *THIS JOURNAL*, **60**, 1857 (1938).

(4) Rao and Samuel, *Current Sci.*, **3**, 549 (1935).