85 g. (0.5 mole) of α-acetoxy-α,γ-dimethylvaleronitrile (X) was added dropwise to the pyrolysis tube heated at 375°. The pyrolysate was worked up as indicated previously for that from the pyrolysis of VII. (Titration of an aliquot of the aqueous extracts indicated that 55% of the theoretical amount of acetic acid had been liberated.) The ether extract was fractionally distilled through a 10-in., helix-packed column to yield 25 g. (46%) of α-isobutylacrylonitrile (XI), b.p. 68° (50 mm.), n_D^{25} 1.4232, and 33 g. of the starting acetate X. The yield of XI, based on unrecovered starting material, was 77%.

Anal. Calcd. for $C_7H_{11}N$: C, 77.06; H, 10.09. Found: C, 77.08; H, 9.85.

Polymerization of α-isobutylacrylonitrile (XI). By the use of a procedure similar to that described for α-*n*-propylacrylonitrile (VIII), 4 g. of α-isobutylacrylonitrile (XI) was polymerized in an emulsion system over a 4-day period. The crude polymer, formed by coagulation in methanol, was redissolved in tetrahydrofuran and was then reprecipitated by the addition of this solution to methanol. The white powder was dried under vacuum to yield 0.4 g. (10%) of poly-α-isobutylacrylonitrile, softening point 50–54°, $[\eta]_{c\to 0}$ 0.1.

Copolymerization of α-isobutylacrylonitrile (XI) *and methyl methacrylate.* By a procedure similar to that described for the polymerization of α-*n*-propylacrylonitrile (VIII), 2 g. of α-isobutylacrylonitrile and 3 g. of methyl methacrylate were copolymerized over a 52-hr. period. The emulsion was poured into 200 ml. of methanol and the mixture was made acidic to litmus. After the copolymer was collected by filtration, it was redissolved in 10 ml. of tetrahydrofuran and reprecipitated by the addition of this solution to 100 ml. of methanol. The copolymer was dried under vacuum to yield 0.3 g. of a white powder, softening point 115–145°, $[\eta]_{c\to 0}$ 0.3. Analysis showed that the copolymer contained 3.97% nitrogen, which indicated that the copolymer contained approximately 1 mole of α-isobutylacrylonitrile for every 2 moles of methyl methacrylate.

α-Acetoxy-α-methylcaprylonitrile (XIII). Methyl *n*-hexyl ketone cyanohydrin (XII), b.p. 130° (11 mm.), n_D^{25} 1.4301 [reported[11f] b.p. 131–132° (11 mm.), n_D^{20} 1.43227], was prepared in a 58% yield by a modification of the procedure described above for the preparation of methyl ethyl ketone cyanohydrin (II). By the same procedure described above for the preparation of α-acetoxy-α-methylvaleronitrile (VII), 90 g. (0.58 mole) of the cyanohydrin XII was acetylated with 70 g. (0.89 mole) of acetyl chloride to yield 100 g. (90%) of α-acetoxy-α-methylcaprylonitrile (XIII), b.p. 128° (12 mm.), n_D^{25} 1.4286.

Anal. Calcd. for $C_{11}H_{19}NO_2$: C, 67.01; H, 9.65. Found: C, 66.99; H, 9.38.

α-n-Hexylacrylonitrile (XIV). At the rate of 3 g. per min., 71 g. (0.38 mole) of α-acetoxy-α-methylcaprylonitrile (XIII) was added dropwise to the pyrolysis tube heated at 375°, as described above. The pyrolysate was worked up as described for the *n*-propylacrylonitrile (VIII). (Titration of an aliquot of the aqueous extracts indicated that 48% of the theoretical amount of acetic acid had been liberated.) The ether extract was fractionally distilled through a 10-in., helix-packed column to yield 24.5 g. (48%) of α-*n*-hexylacrylonitrile (XIV), b.p. 114° (50 mm.), n_D^{25} 1.4347 [reported b.p. 80° (12 mm.),[11f] b.p. 201° (766 mm.),[11f] b.p. 112° (48 mm.),[12] n_D^{20} 1.43972,[11f] n_D^{20} 1.4350[12]], and 35 g. of the starting acetate XIII. The yield of XIV, based on unrecovered starting material, was 92%.

Anal. Calcd. for $C_9H_{15}N$: C, 78.83; H, 10.95. Found: C, 79.11; H, 10.71.

Polymerization of α-n-hexylacrylonitrile (XIV). By a procedure very similar to that described for α-*n*-propylacrylonitrile (VIII), 5 g. (0.036 mole) of α-*n*-hexylacrylonitrile (XIV) was polymerized in an emulsion system over a 4-day period. The polymer was purified as described above to yield 0.3 g. of a clear viscous poly-α-*n*-hexylacrylonitrile, $[\eta]_{c\to 0}$ 0.11, which became a hard glass at 0° and resoftened at 15–18°.

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[CONTRIBUTION FROM THE SOUTHERN REGIONAL RESEARCH LABORATORY[1]]

Kinetics of Diels-Alder Reactions of Eleostearic Acids with Maleic Anhydride and Substituted Maleic Anhydrides

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The kinetics of the Diels-Alder reactions of *alpha-* and *beta*-eleostearic acids with chloromaleic, methylmaleic, and maleic anhydrides have been investigated. The reactions of chloromaleic anhydride and maleic anhydride with the eleostearic acids conformed to second order kinetics, but those of methylmaleic anhydride particularly with *alpha*-eleostearic acid, were not strictly second order. The specific rate constants for the Diels-Alder reactions of *beta*-eleostearic acid were found to be of greater magnitude than those for *alpha*-eleostearic acid, and the reactions of the former were found to be less temperature-dependent than the reactions of the latter. Energies of activation for the systems in which *beta*-eleostearic acid was a reactant were markedly lower than those for systems containing *alpha*-eleostearic acid, while the magnitude of the frequency factors of the respective systems was reversed. Substitution of either a methyl group or chlorine atom into maleic anhydride resulted in diminished dienophilic activity. The influences of structure, steric requirements, and group inductive effects on the specific rate constants of the various reactions have been considered.

In continuing the study of the Diels-Alder reactions of *alpha-* and *beta*-eleostearic (octadecatrienoic) acids[2,3] we have now investigated the kinetics of their reactions with maleic anhydride, chloromaleic anhydride, and methylmaleic anhydride (citraconic anhydride). This series of dienophiles

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[1] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

[2] J. S. Hoffman, R. T. O'Connor, F. C. Magne, and W. G. Bickford, *J. Am. Oil Chemists' Soc.*, **32**, 533 (1955).

[3] J. S. Hoffmann, R. T. O'Connor, F. C. Magne, and W. G. Bickford, *J. Am. Oil Chemists' Soc.*, **33**, 410 (1956).

is of particular interest, because it provides a means of comparing the effects of electron-withdrawing and electron-releasing substituents on the rates of Diels-Alder addition. Of further interest is a comparison of the relative rates of addition of such dienophiles to *alpha*-eleostearic acid, which contains only one pair of conjugated, *trans,trans* ethylenic bonds, with rates of addition to *beta*-eleostearic acid, which contains two pairs of such double bonds—having one ethylenic bond in common.

Previous work has shown that the 9-*cis*, 11-*trans*, 13-*trans* conjugated system of *alpha*-eleostearic acid forms a single maleic anhydride adduct across carbons 11–14. However, two maleic anhydride adducts are produced with the all *trans* system of *beta*-eleostearic acid, addition occurring either across carbons 9–12 or carbons 11–14.[4]

Accordingly, an investigation was undertaken to determine the influence of temperature, diene configuration, dienophile structure, and group inductive effects on the specific rate constants of the various reactions.

EXPERIMENTAL

Preparation of materials. Alpha- and beta-eleostearic acids. Pure *alpha*- and *beta*-eleostearic acids were prepared by the method of Hoffman, *et al.*[5] *Alpha*-eleostearic acid: m.p. 49.2–49.4°, absorptivity (a) = 176.7 at 271.5 mμ in cyclohexane. *Beta*-eleostearic acid: m.p. 71–72°, absorptivity (a) = 201.8 at 269.0 mμ in cyclohexane.

Maleic anhydride. Maleic anhydride was crystallized from chloroform (2 g./ml.) at room temperature (m.p. 51–53°).

Chloromaleic anhydride. Chloromaleic anhydride was placed in the refrigerator until it partially solidified. The crystals were filtered, washed with petroleum ether, dissolved in ethyl ether (1 g./ml.), and allowed to crystallize at −20° (m.p. 31–32°).

Methylmaleic anhydride. Methylmaleic anhydride was purified by high vacuum distillation (b.p. 35°/100μ).

Xylene. Reagent grade xylene was washed with concentrated sulfuric acid until no discoloration was produced, then with water, and finally with a solution of potassium hydroxide. The washed xylene was dried first with anhydrous sodium sulfate, and then with solid potassium hydroxide before it was distilled (b.p. 137–138°).

Determination of reaction rates. A 2.78-g. sample of pure eleostearic acid (0.01 mole) was dissolved in approximately 40 ml. of purified xylene. To this solution was added 50.0 ml. of a 0.20*M* solution of the dienophile, and the volume made up to 100.0 ml., thus resulting in an equimolar mixture of reactants (0.10*M*).

After the reactants were mixed thoroughly, aliquots (*ca.* 5 ml.) were poured rapidly into a number of small screw cap test tubes. The caps, which contained fresh aluminum foil liners over their rubber gaskets, were tightened, and the tubes immediately immersed in a constant temperature bath controlled within ±0.1° of the desired temperature.

The tubes were removed at regular intervals, rapidly cooled to room temperature, and the contents immediately analyzed. The course of the reaction was followed by the disappearance of eleostearic acid, as determined spectrophotometrically.[5]

Using the above described procedure, at least three independent experiments, employing freshly prepared reagents, were carried out at each of two temperatures[6] for the various diene-dienophile systems. Generally, seven eleostearic acid determinations were made for each run at various time intervals during the course of each reaction, thereby providing a minimum of 21 values for use in determining the specific rate constants for each system at a given temperature. Conversion of the reactants into Diels-Alder adducts ranged from about 30–55%, depending upon the temperature and system employed.

Treatment of data. Since the diene and dienophile were employed in equimolar concentrations, it was possible to examine the data for conformity to a second order reaction by plotting the reciprocal of the concentration *vs.* time. Such graphs of the data obtained for the reactions of the eleostearic acids with maleic anhydride and chloromaleic anhydride were linear, indicating the reactions to be second order. However, the methylmaleic anhydride reactions, particularly with *alpha*-eleostearic acid, showed deviations from second order kinetics. All of the data obtained for each diene-dienophile system at a given temperature were combined, and the method of least squares was applied to the data. In these equations of the form $\frac{1}{C} = at + b$, where C is the molar concentration and t is time in minutes, the slope, a, gave the specific reaction rate constant, k. These constants are tabulated in Table I. For each diene-dienophile system, the values of the specific rate constants at two different temperatures were used to calculate the energies of activation from the Arrhenius equation. The energy of activation, E, was obtained from the slope of the equation $\ln k = \frac{-E}{RT} + \ln A$. These energies of activation and A parameters are presented in Table II. Even though five rate runs were made at each of two temperatures for the methylmaleic anhydride–*alpha*-eleostearic acid system, no significant differences could be found in the rates at these two temperatures.

TABLE I

SECOND ORDER RATE CONSTANTS FOR DIELS-ALDER REACTIONS

Reaction	Reaction Temp., °C.	10^5k^a
Maleic anhydride + α-eleostearic acid	70	20
	85	56
Maleic anhydride + β-eleostearic acid	55	34
	70	74
	85	153^b
Chloromaleic anhydride + α-eleostearic acid	85	21
	100	62
Chloromaleic anhydride + β-eleostearic acid	85	117
	100	244
Methylmaleic anhydride + β-eleostearic acid	85	8^b
	100	15
	115	27

[a] Units for k are l. mole^{-1} sec.$^{-1}$ [b] Value calculated for 85°.

DISCUSSION

Diels-Alder reactions are first order with respect to both diene and dienophile components,[7,8] al-

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(4) W. G. Bickford, E. F. DuPré, C. H. Mack, and R. T. O'Connor, *J. Am. Oil Chemists' Soc.*, **30**, 376 (1953).

(5) J. S. Hoffmann, R. T. O'Connor, D. C. Heinzelman, and W. G. Bickford, *J. Am. Oil Chemists' Soc.*, **34**, 338 (1957).

(6) Data obtained at two temperatures were considered adequate for the close approximation of the Arrhenius parameters for the various reactions.

TABLE II

ARRHENIUS PARAMETERS FOR THE DIELS-ALDER REACTIONS

Reaction	E_1 kcal. mole^{-1}	log A[a]
Maleic anhydride + α-eleostearic acid	17	7.0
Maleic anhydride + β-eleostearic acid	12	4.3
Chloromaleic anhydride + α-eleostearic acid	19	8.0
Chloromaleic anhydride + β-eleostearic acid	13	5.0
Methylmaleic anhydride + β-eleostearic acid	12	3.0

[a] Units for A are l. mole^{-1} sec.$^{-1}$

though recent work has shown that this is not strictly the case in instances where a large excess of dienophile is employed in the reaction.[9] Diene syntheses are reversible, and the reverse reaction is unimolecular.[10] The pre-exponential factor of the Arrhenius Equation, $k = Ae^{-E/RT}$, is of the order of 10^{12} sec.$^{-1}$ for the reverse reaction, which is of the same magnitude as that of "normal" first order reactions. For Diels-Alder reactions the magnitude of the parameter, A, of the Arrhenius Equation is generally many powers of 10 lower than the collision frequency of 10^{11} l. mole^{-1} sec.$^{-1}$, which is characteristic of "normal" bimolecular reactions. Since the probability of electron transition from one quantum state to another is the same for both forward and reverse reactions,[10] it may be concluded that the low values of A found for Diels-Alder reactions are due to structural complexities of the molecules employed in these reactions rather than to rate-restricting transitions.

It may be presumed *a priori* that structural variations among closely related dienes or dienophiles will be reflected in the relative magnitudes of the pre-exponential factors for related Diels-Alder reactions. That is, the fraction of collisions between activated molecules resulting in adduct formation will be dependent upon the internal degrees of freedom and steric requirements of the reactants.

Theories of electronic effects in Diels-Alder reactions have been applied chiefly to the interpretation of the structures of unsymmetrical adducts. However, recent investigations have shown that electronic effects in both the diene and dienophile components markedly influence the rate of the Diels-Alder reaction.[9,11] Substitution of strongly electron-withdrawing groups into the dienophile enhances dienophilic activity, while a similar effect is observed on the reaction rate through substitution of electron-releasing groups in the diene. Although the process by which electrons are transferred from the diene to the dienophile is not fully understood as yet, it is apparent that the transition state intermediate has some polar characteristics, that the reactants lie in parallel planes,[9,12] and that the two new *sigma* carbon to carbon bonds are formed simultaneously.[13,14] In this connection, it is of particular interest to note the sensitivity of the energy of activation to inductive effects of substituents in both the diene and dienophile as observed by Andrews and Keefer.[9] It may be presumed that electronic effects in the Diels-Alder reaction due to variation of substituents may be reflected in differences found in the energies of activation for closely related systems.

An increase in temperature has a greater effect on the change of reaction rate in those system employing *alpha*-eleostearic acid than in the *beta*-eleostearic acid systems. It was observed that, on raising the reaction temperature 15°, the rates of reaction for *beta*-eleostearic acid with the dienophiles employed are approximately doubled, while those for *alpha*-eleostearic acid are about trebled (see Table I).

The Arrhenius parameters for the various reactions are presented in Table II. Inspection of these data reveals that the energies of activation for all the systems containing *beta*-eleostearic acid are lower than those for the corresponding *alpha*-eleostearic acid systems.

The energies of activation for systems in which chloromaleic anhydride was a reactant are somewhat higher (1–2 kcal./mole) than for those systems employing maleic anhydride. It is of interest to note that differences in E of a similar magnitude were obtained with these same dienophiles when employed with anthracene and dimethylanthracene.[9] The energy of activation of the reaction of methylmaleic anhydride with *beta*-eleostearic acid appears to be equivalent to that of the analogous reaction with maleic anhydride, although the accuracy of the former value is questionable for reasons previously mentioned.

In considering the pre-exponential factor A for the various reactions, it is well to bear in mind that this factor contains an entropy term. The A factors for the *alpha*-eleostearic acid systems are definitely higher than those for the corresponding *beta*-eleostearic acid systems. This indicates that there are more successful collisions between activated molecules in systems containing *alpha*-eleostearic acid than in systems containing *beta*-eleostearic acid.

The fundamental difference between *alpha*- and *beta*-eleostearic acids lies in the fact that the 9, 10

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[11] J. J. Dudkowski and E. I. Becker, *J. Org. Chem.*, **17**, 201 (1952).

[12] W. Rubin and A. Wassermann, *J. Chem. Soc.*, **1950**, 2205.

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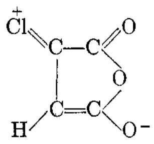
ethylenic linkage of the former has a *cis* configuration, while that of the latter has a *trans* configuration. This structural difference has a marked effect on the relative rates of reaction of the two acids. The data in Table I illustrate this point in that the presence of an additional *trans* ethylenic bond in *beta*-eleostearic acid results in higher values of k (*ca.* 4 times as great) for the reacting systems than does the presence of a corresponding *cis* bond in *alpha*-eleostearic acid. A similar observation has been made in the dimerization of eleostearic acids through a Diels-Alder mechanism.[15] The probability of the occurrence of an s-*cis* configuration in *beta*-eleostearic acid, owing to the all *trans* arrangement of its conjugated triene system, is without doubt greater than that for a similar occurrence in the *cis, trans, trans* conjugated system of *alpha*-eleostearic acid, thus enhancing the rate of adduct formation of the former. However, this explanation does not appear entirely adequate to account for the observed differences in the rates of addition of these two acids to the dienophiles. It is possible that the replacement of a *cis* ethylenic bond by a *trans* in the triene systems of the acids results in a lower "para-localization energy"[16] in the localization of two *pi* electrons in the 1, 4 positions of the remaining conjugated diene.

The dienophiles employed are closely related structurally, and the effect of substituent groups on the rate of reaction may be observed most readily by a comparison of the relative rates of reaction at one given temperature. Thus, the relative k values (in parentheses, and derived from data in Table I) are in the order maleic anhydride + *beta*-eleostearic acid (19.1), chloromaleic anhydride + *beta*-eleostearic acid (14.6), maleic anhydride + *alpha*-eleostearic acid (7.0), chloromaleic anhydride + *alpha*-eleostearic acid (2.6), methylmaleic anhydride + *beta*-eleostearic acid (1.0). Introduction of either chlorine or a methyl group into maleic anhydride reduces dienophilic activity. This type of phenomenon has been attributed, in part, to space restrictions imposed by the substituent groups 6, 16, 17.[7,17,18] However, inspection of scale models shows that the facile approach of the substituted maleic anhydrides to the eleostearic acids is not less favored than that of maleic anhydride itself. Moreover, the steric requirements of the methyl group and chlorine are approximately the same, hence it does not seem reasonable to account for the lower activity of methylmaleic anhydride on a steric basis. The influence of the methyl group on the reaction rate is that which would be expected from group inductive effects. On the other hand, it would be expected that the effect of substitution of a chlorine atom into maleic anhydride would result in an enhancement of its dienophilic activity over that of maleic anhydride. The diminished activity of chloromaleic anhydride has been attributed to a contribution of a resonance form, thus reducing the electrophilic nature of the dienophile.[9] Further support for this viewpoint is



to be found in our observation (unpublished data) that dichloromaleic anhydride is practically inactive as a dienophile when employed with the eleostearic acids. It would be expected that dichloromaleic anhydride would be more highly resonance-stabilized and consequently less active as a dienophile than the mono-chloro compound.

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