TABLE VI

TEMPERATURE DEPENDENCE

Expt.	Solvent	Acid	E, kcal. mole^{-1}	log A
11, 17, 20	Dioxane	CH_3COOH (Excess)	18.5 ± 0.2	9.11 ± 0.15
24, 26, 27	95% EtOH	$HClO_4$	$20.6 \pm .3$	$12\ 08 \pm\ 2$
45, 46, 66	Dioxane 2.77% H_2O	$HClO_4$	$23.7 \pm .2$	$14.61 \pm .15$

Since the reaction is fastest in dioxane with perchloric acid and slowest in dioxane with excess acetic acid, it is apparent that the activation energies vary in just the opposite order. The activation energy is highest in the fastest solvent, but the large increase in the frequency factor outweighs the unfavorable energy effect by far.

Similar behavior with such reactions as the alkaline hydrolysis of ethyl benzoate, methylation of pyridine, etc., was studied by Fairclough and Hinshelwood.[9] It does seem qualitatively plausible that, in a reaction with a charged intermediate, increased solvation will lower the energy of the intermediate, but will magnify steric requirements and thus lead to lower values of A.

The bimolecular reaction with perchloric acid is seen to be quite fast, A ranging from 10^{12} to 10^{14} l. mole^{-1} sec.$^{-1}$, in agreement with the simple mechanism originally proposed. This facilitates the application to the wider problem of aromatic substitution which is discussed in a subsequent publication.

Acknowledgment.—F. K. is happy to acknowledge a generous grant-in-aid from the Hynson, Westcott, and Dunning Fund.

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[9] R. A. Fairclough and C. N. Hinshelwood, *J. Chem. Soc.*, 538, 1573 (1937); 236 (1938); 598 (1939).

ABERDEEN, MARYLAND

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA AT DAVIS]

A Kinetic Study of the Diels–Alder Reaction of Various Anthracene and Maleic Anhydride Derivatives

BY L. J. ANDREWS AND R. M. KEEFER

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The rates of reaction of anthracene and dimethylanthracene with maleic anhydride and several of its substitution products have been followed by colorimetric procedures. In the presence of a large excess of dienophile the reactions in chloroform are first order with respect to diene, but the first-order rate constants are not directly proportional to dienophile concentration. This kinetic behavior can be explained quantitatively through consideration of the fact that a substantial fraction of the diene in the reaction mixtures is bound in a molecular complex with the dienophile. The mechanism of the reaction is discussed in the light of these observations and in terms of the effects of changes in temperature, solvent and substituents in the reactant molecules on the reaction rates. The possibility that Diels–Alder adduct may form by reaction of the diene–dienophile complex with a second dienophile molecule has been ruled out on the basis of rate studies.

The results of previous kinetic studies indicate that the Diels–Alder reaction is first order with respect to both the diene and dienophile.[1] The reaction often is accompanied by the transitory formation of highly colored molecular complexes of the two reactants, and it has been suggested that these complexes are necessary precursors of the adducts.[2] In view of what is known concerning the rate laws of other reactions in which molecular complex formation is an adjunct to the formation of stable products,[3] it seems likely that the kinetics of the Diels–Alder reaction may, in some cases, be more complex than earlier investigations have revealed.

This matter has now been explored through a study of the rates of reaction of anthracene and dimethylanthracene with maleic anhydride and some of its derivatives in chloroform and other solvents at several temperatures. These compounds have been chosen for study since, in the vicinity of room temperature, they display a marked tendency to form complexes[4] and undergo essentially irreversible Diels–Alder reaction at measurable rates. The mechanistic significance of the effects of changes in structure of diene and dienophile components on these reaction rates has been considered.

The Reactions in Chloroform.—In all rate runs the concentration of the dienophile was in large excess over that of the diene. The rate of disappearance of the diene to form the Diels–Alder adduct was followed by measuring (on the Beckman spectrophotometer) the changes in solution color with time. This color, which results from a composite of the absorptions of the diene and diene–dienophile complex, initially was reddish-orange in the runs with dimethylanthracene and yellow in those with anthracene. Primary attention was given to the reactions of dimethylanthracene with maleic anhydride and chloromaleic anhydride, both of which occur rapidly in chloroform to yield the colorless substituted succinic anhydride derivatives.

Rate constants, k (see Table I), were evaluated for individual runs on the assumption that equation 1 accounted for the change in optical density, d, of the reaction mixtures with time.

$$2.303 \log \frac{[(\mathrm{ArH})_T]_i}{[(\mathrm{ArH})_T]_t} = 2.303 \log \frac{d_i}{d_t} = k(\mathrm{D})t \quad (1)$$

The term $(\mathrm{ArH})_T$ represents the total concentration (both free and complexed) of the diene, and (D) is

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[1] See, for example (a) A. Wassermann, *J. Chem. Soc.*, 828 (1935); (b) W. E. Bachmann and L. B. Scott, THIS JOURNAL, **70**, 1458 (1948).

[2] See M. C. Kloetzel, "Organic Reactions," Vol. IV, John Wiley and Sons, Inc., New York, N. Y., pp. 8 and 9, for a summary.

[3] (a) R. M. Keefer and L. J. Andrews, THIS JOURNAL, **75**, 543 (1953); **76**, 253 (1954); (b) L. J. Andrews and R. M. Keefer, *ibid.*, **75**, 3557 (1953); (c) R. M. Keefer, J. H. Blake and L. J. Andrews, *ibid.*, **76**, 3062 (1954).

[4] L. J. Andrews and R. M. Keefer, *ibid.*, **75**, 3776 (1953).

the dienophile concentration, a constant in any individual run. The subscripts i and t refer, respectively, to times initial and *t*.

TABLE I

SECOND-ORDER RATE CONSTANTS FOR THE DIELS-ALDER REACTIONS IN CHLOROFORM SOLUTION

(D), mole/l.	$[(ArH)_T]_i$, mole/l. × 10^3	10^3k, mole^{-1} l. sec.$^{-1}$	λ,[a] mμ	Temp., °C.
Maleic anhydride–dimethylanthracene				
0.0200	0.97	68.5	410	25.2
.0500	.97	68.1	410	25.2
.100	.97	67.3	410	25.2
.188	24.9	68.4	450	25.2
.200	0.97	67.0	410	25.2
.250	33.2	67.1	450	25.2
.300	29.9	65.4	450	25.2
.500	33.2	61.5	450	25.2
.500	0.97	60.4	410	25.2
1.002	33.2	57.4	450	25.2
1.202	1.99	52.5	410	25.2
1.414	3.51	49.3	410	25.2
0.0408	1.00	22.1	410	2.2
0.0816	0.50	22.2	400	2.2
Chloromaleic anhydride–dimethylanthracene				
0.169	7.53	11.3	450	25.2
.338	15.1	9.71	450	25.2
.676	10.0	9.02	450	25.2
1.015	2.51	8.18	450	25.2
1.015	5.0	8.16	450	25.2
1.015	10.0	8.35	470	25.2
1.353	5.0	7.44	450	25.2
0.169	13.0	2.72	450	2.4
.338	15.7	2.45	450	2.4
Maleic anhydride–anthracene				
0.206	23.0	0.0337	430	25.2
.412	17.2	.0310	430	25.2
.824	57.4	.0280	430	25.2
.206	23.1	.156	430	45.5
.412	17.3	.133	430	45.5
.824	57.8	.118	430	45.5
Chloromaleic anhydride–anthracene				
0.824	5.68	0.00273	450	25.2
0.829	0.91	0.0156	408	46.5
Citraconic anhydride–dimethylanthracene				
0.465	10.0	0.0565	440	25.2
0.93	5.0	0.0410	440	25.2

[a] Wave lengths at which individual runs were followed.

In general the second-order rate constant for these reactions decreases as the dienophile concentration increases. The rate variation may be accounted for quantitatively in terms of the changes in ratio of free to complexed diene with changes in dienophile concentration. At all times the concentrations of free and complexed diene which are in equilibrium (see equation 2), are related by expression 3.

$$\mathrm{ArH} + \mathrm{D} \overset{K_1}{\rightleftarrows} \mathrm{ArH{\cdot}D} \quad K_1 = (\mathrm{ArH{\cdot}D})/(\mathrm{D})(\mathrm{ArH}) \quad (2)$$

$$(\mathrm{ArH})_T = (\mathrm{ArH}) + (\mathrm{ArH{\cdot}D}) = (\mathrm{ArH}) + K_1(\mathrm{D})(\mathrm{ArH}) \quad (3)$$

Two experimentally indistinguishable processes, 4 or 5, may serve as the rate-determining step[5] in the formation of the Diels–Alder adduct.

$$\mathrm{D} + \mathrm{ArH} \xrightarrow{k_1} \text{adduct} \quad (4)$$

$$\mathrm{ArH{\cdot}D} \xrightarrow{k_1'} \text{adduct} \quad (5)$$

If it is assumed arbitrarily that step 4 is rate determining, then it follows from equation 6 and the differential form of equation 1 that the experimentally determined rate constants, *k*, are related to the complex equilibrium constant K_1 by equation 7

$$\frac{d\,(\text{adduct})}{dt} = \frac{-d(\mathrm{ArH})_T}{dt} = \frac{k_1(\mathrm{ArH})_T(\mathrm{D})}{1 + K_1(\mathrm{D})} \quad (6)$$

$$1/k = 1/k_1 + K_1(\mathrm{D})/k_1 \quad (7)$$

If the treatment of equations 1–5 correctly explains the observed rate variations with changes in dienophile concentration, plots of $1/k$ *vs.* (D) should give straight lines of slope K_1/k_1 and intercept $1/k_1$. Figure 1 presents such a graphical interpretation of the data for the reactions of dimethylanthracene with both maleic anhydride and chloromaleic anhydride at 25°. From these linear plots values of $k_1 = 0.0706$ mole^{-1} l. sec.$^{-1}$ and $K_1 = 0.294$ l. mole^{-1} for the maleic anhydride reaction and $k_1 = 0.0148$ mole^{-1} l. sec.$^{-1}$ and $K_1 = 0.398$ l. mole^{-1} for the chloromaleic anhydride reaction have been calculated.

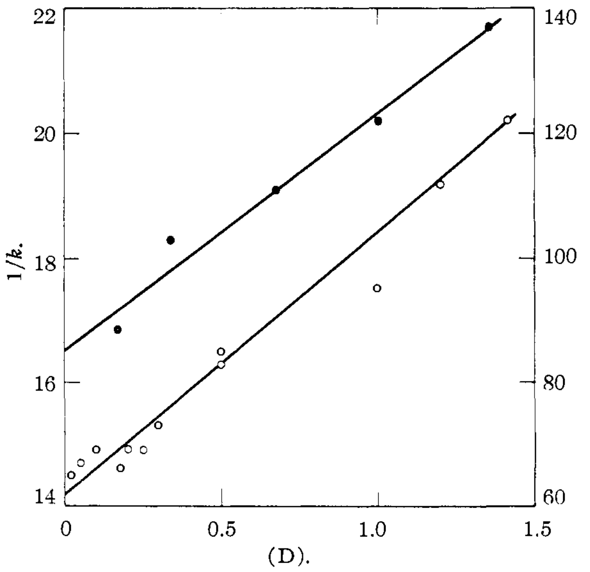

Fig. 1.—The variation in *k* for dimethylanthracene with dienophile concentration (chloroform, 25.2°). The lower curve (left-hand ordinates) gives data for (D) = maleic anhydride. The upper curve (right-hand ordinates) is for (D) = chloromaleic anhydride.

The equilibrium constant for the interaction of dimethylanthracene and maleic anhydride was also evaluated directly (as described in the Experimental section) from the initial optical densities at 450 mμ of a series of freshly prepared chloroform solutions of the two components. The value thus obtained, $K_1 = 0.242$ mole^{-1} l., was in reasonably good agree-

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[5] If one chooses equation 5 as the rate-determining step, the subsequent treatment (equations 6 and 7) may be corrected by the substitution of $k_1'K_1$ for k_1.

ment with that determined from analysis of the rate data by equation 7.

These constants were considerably less than that reported previously[4] for the anthracene–maleic anhydride complex but were of the same order of magnitude as those obtained in this investigation for a number of structurally related complexes. Table II lists K_1 values for complexes of several anthracene and maleic anhydride derivatives which were measured (see equation 16 of the Experimental section) by spectrophotometric evaluation of the complex concentrations under equilibrium conditions. Extinction coefficients for the interaction products at the several wave lengths at which measurements were made are included in Table II. The previous value for the anthracene–maleic anhydride complex was based on the results of measurements of solutions in which only small fractions of the two components were complexed, and is undoubtedly erroneous.

TABLE II

EQUILIBRIUM CONSTANTS FOR COMPLEX FORMATION IN CHLOROFORM SOLUTION

λ, mμ	K_1, mole^{-1} l.	$\epsilon_{ArH \cdot D}$	λ, mμ	K_1, mole^{-1} l.	$\epsilon_{ArH \cdot D}$
Maleic anhydride–anthracene at 25.2°			Maleic anhydride–anthracene at 2.3°		
420	0.296	725	420	0.408	625
430	.303	550	430	.391	520
440	.342	385	440	.419	385
450	.335	285	450	.423	285
Chloromaleic anhydride–anthracene at 25.2°			Citraconic anhydride–dimethylanthracene at 25.2°		
410	0.264	1100	430	0.354	950
420	.281	1000	440	.352	720
430	.283	930	450	.373	530
440	.308	790	460	.386	385
450	.304	700	470	.430	255
Maleic anhydride–dimethylanthracene at 25.2°			Chloromaleic anhydride–dimethylanthracene at 25.2°		
[a]	0.294	..	[a]	0.398	..
450[b]	0.242	1100			

[a] The equilibrium constant as evaluated by graphical interpretation of rate data by equation 7. [b] The equilibrium constant evaluated from the initial optical densities obtained by extrapolation of the rate data to the time of mixing.

The Variations in Rate with Changes in Reactant Structure.—In the process of molecular complex formation involving aromatic systems one component, in this instance the aromatic hydrocarbon, is presumed to share its π electrons to some degree with a second molecule (the dienophile) which has the properties of a Lewis acid.[6] While the exact mechanism of electron transfer between the diene and dienophile components in the formation of the Diels–Alder adduct is not clear,[7] the process apparently has some polar character. Thus the same substituents which often measurably enhance the basic character of the aromatic component of a molecular complex enhance the reactivity of a diene in adduct formation. For example, present and previous[8] work shows that 9-methyl- and 9,10-dimethylanthracene form adducts more rapidly than does anthracene. Strongly electron withdrawing groups which, as acceptor substituents, may promote molecular complex formation[6] also increase Diels–Alder reactivity of dienophiles.[9] It is interesting in this regard that the electron transfers leading to aromatic complex formation and to formation of the transition state intermediate in the Diels–Alder reactions very likely require similar structural arrangements in which the two interacting molecules lie in parallel planes.[10]

The effects of the donor and acceptor substituents on the position of the maleic anhydride–anthracene complex equilibrium are, as revealed by this investigation, small. The variations in K_1 for the several complexes reported in Table II are barely outside the range of experimental error.

The rate of formation of Diels–Alder adduct is much more sensitive to substituent effects. An approximate comparison of the relative magnitudes of k_1 values (equation 4) for adduct formation may be made in terms of the relative magnitudes of k values of Table I (measured at about the same dienophile concentrations). The relative k values (in parentheses) for the several reactions in the concentration range (D) = 0.8–1.0 M are in the order maleic anhydride–dimethylanthracene (21,000) > chloromaleic anhydride–dimethylanthracene (3000) > citraconic anhydride–dimethylanthracene (15) > maleic anhydride–anthracene (10) > chloromaleic anhydride–anthracene (1.0).

Both chloro and methyl substituents reduce dienophile reactivity. The effect of the methyl group on the reaction rate appears normal, but that of the chloro substituent is opposite to that which would be predicted for a reaction which proceeds through a polar transition state intermediate from a consideration of group inductive effects. The low reactivity of both methyl and halogen (bromine) substituted maleic anhydrides with respect to the formation of anthracene adducts has previously[11] been treated as a steric problem. An examination of molecular models reveals no convincing evidence that the close approach of chloromaleic anhydride to the anthracene nucleus is less favored than is the corresponding approach of maleic anhydride. Halogen and methyl groups, which are of similar dimensions, might (if they imposed a size restriction on dienophile reactivity) also be expected to offer steric inhibition to adduct formation when substituted in the diene component. Yet 9,10-dimethyl-

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(6) L. J. Andrews, *Chem. Revs.*, **54**, 713 (1954).

(7) For a summary of various interpretations see (a) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 711–721. (b) R. D. Brown, *J. Chem. Soc.*, 3129 (1951), and preceding papers.

(8) W. E. Bachmann and M. C. Kloetzel, THIS JOURNAL, **60**, 481 (1938).

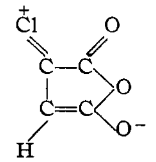
(9) (a) F. Bergmann and H. E. Eschinazi, *ibid.*, **65**, 1405 (1943); (b) J. J. Dudkowski and E. I. Becker, *J. Org. Chem.*, **17**, 201 (1952).

(10) W. Rubin and A. Wassermann, *J. Chem. Soc.*, 2205 (1950), present kinetic evidence for such a transition state configuration in the reactions of cyclopentadiene with benzoquinone and chloranil. The results of X-ray crystallographic measurements and studies of dichroism of molecular complexes (*viz.*, hexamethylbenzene–chloranil) strongly favor a pancake configuration for the two components (see (a) H. M. Powell and G. Huse, *J. Chem. Soc.*, 435 (1943); (b) H. M. Powell, G. Huse and P. W. Cooke, *ibid.*, 153 (1943); (c) K. Nakamoto, THIS JOURNAL, **74**, 1739 (1952)).

(11) (a) W. E. Bachmann and L. B. Scott, *ibid.*, **70**, 1458 (1948); (b) W. R. Vaughan and K. M. Milton, *J. Org. Chem.*, **16**, 1748 (1951).

anthracene is considerably more reactive than anthracene. A steric argument *may* correctly explain the low reactivity of *meso*-diethylanthracenes.[12,13]

An alternative explanation for the low reactivity of chloromaleic anhydride is formulated on the assumption that the electrophilic character of this dienophile is reduced through contribution of a form of the type to its structure. Dipole moment and electron diffraction studies show that in simple vinyl halides the carbon–chlorine bond has considerable double bond character.[14]



Temperature Effects on Reaction Rates.—Further evidence which seems to minimize the importance of steric effects of diene and dienophile substituents in controlling the relative rates of the several reactions reported in Table I was obtained through interpretation of the effects of temperature changes on the reaction rates. Values of the pre-exponential factors (A) and the energies of activation (E_a) corresponding to equation 8 are given in Table III along with the corresponding entropies of activation for the various reactions. The values of k_1 required for these calculations were deduced from k and K_1 values (Tables I and II by use of equation 7). The constants K_1 in the vicinities of 2 and 45° were calculated from K_1 values obtained at 25° on the assumption that ΔH for complex formation was -1.8 kcal. This figure was derived from reported constants (Table II) for the maleic anhydride–anthracene equilibrium at 25.2 and 2.3°.[15] The rather large variations in rate constants for the reactions covered by Table I result primarily from differences in E_a rather than A values. In other words the entropy losses attending formation of the several transition state intermediates are closely similar.

$$k_1 = Ae^{-E_a/RT} \qquad (8)$$

TABLE III

ARRHENIUS PARAMETERS AND ENTROPY OF ACTIVATION FOR THE DIELS-ALDER REACTIONS IN CHLOROFORM SOLUTION

Reaction	$\log_{10} A^a$	E_a, kcal.	$-\Delta S$, e.u.
Maleic anhydride + dimethylanthracene	4.7	8.0	39
Maleic anhydride + anthracene	5.2	13.1	37
Chloromaleic anhydride + dimethylanthracene	5.4	9.8	36
Chloromaleic anhydride + anthracene	5.4	15.2	36

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

Solvent Effects.—The rates of reaction of maleic anhydride and dimethylanthracene in several solvents of varying polarity are recorded in Table IV. The reactions are slower in acetic acid and acetone than in chloroform and carbon tetrachloride, but, as has been observed previously[7a] for other types of Diels–Alder reactions, the rates are not highly sensitive to solvent variations. It is possible that desolvation energies of both reactants are larger in the polar than in the non-polar media. For reactions such as these, in which the transition state intermediate is probably only weakly polarized, the kinetic advantages of a polar medium may thus be obscured.

TABLE IV

THE EFFECT OF SOLVENT ON THE SECOND-ORDER RATE CONSTANTS FOR THE REACTION OF MALEIC ANHYDRIDE AND DIMETHYLANTHRACENE

Solvent	(D), mole/l.	$[(ArH)_T]_i$, mole/l. $\times 10^3$	10^3k, mole^{-1} l. sec.$^{-1}$	Temp., °C.
Chloroform	0.0200	0.97	69.5	25.2
Carbon tetrachloride	.0199	.96	50.0	25.2
Acetic acid	.0203	.91	25.0	25.2
Acetone	.0200	.99	9.06	25.2
	.250	14.3	10.3	25.2
	.500	9.5	10.3	25.2
	.750	9.5	10.7	25.2
	1.25	4.76	11.0	25.2
	0.130	1.54	1.97	2.0
	.260	1.02	2.07	2.0

The rate constants, k_1, for the reaction at 25.2° in acetone do not show the decrease with increasing dienophile concentration which was observed for the corresponding reaction in chloroform. Apparently the equilibrium constant for formation of the maleic anhydride–dimethylanthracene complex is very small in acetone. This fact also suggests that dissolvation energies of the reactions are relatively high in the polar medium.

The Arrhenius parameters for the reaction in acetone, calculated from the rate constants at 2.0 and 25.2° for solutions of 0.25–0.26 M maleic anhydride concentration, are $\log_{10} A = 6.22$, $E_a = 11.3$ kcal. and $\Delta S^\ddagger = -32$ e.u. The higher value of E_a and the lower value of $\Delta S^\ddagger$ for the reaction in acetone, as compared to that in chloroform, are consistent with the foregoing discussion of reactant solvation energies in the polar and non-polar media.

The Effect of a Foreign Dienophile on the Rate of Complex Formation.—One cannot decide, on the basis of the present results, which of the steps, (4) or (5), is rate determining in adduct formation. The question as to whether or not a diene which is bound in a complex with a dienophile, D, can form an adduct through collision (see equation 9) with a second dienophile molecule, D′, has, however, been tested.

$$\text{Ar H}\cdot\text{D} + \text{D}' = \text{Adduct of ArH and D}' + \text{D} \qquad (9)$$

The results of preceding experiments rule out this possibility for situations in which D and D′ are the

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[12] W. E. Bachmann and J. M. Chemerda, THIS JOURNAL, **60**, 1023 (1938).

[13] This is clearly suggested by the molecular model of 9,10-diethylanthracene. Furthermore the model shows that there is sufficient hindrance to free rotation of the ethyl groups about their bonds to positions 9 and 10 so that both *cis* and *trans* isomers (presumably of widely differing diene reactivity) should exist.

[14] (a) L. O. Brockway, J. Y. Beach and L. Pauling, THIS JOURNAL, **57**, 2693 (1935); (b) J. A. C. Hugill, I. E. Coop and L. E. Sutton, *Trans. Faraday Soc.*, **34**, 1518 (1938); (c) N. B. Hannay and C. P. Smyth, THIS JOURNAL, **68**, 1005 (1946); (d) M. T. Rogers, *ibid.*, **69**, 1243 (1947).

[15] Heats of formation of molecular complexes are generally small and show little variation with minor changes in structures of the components: *cf.* ref. 6, p. 762.

same. Rate studies of the reaction of dimethylanthracene and maleic anhydride in chloroform in the presence of citraconic anhydride, as described below, also indicate that little or no adduct is formed by reaction 9 when D and D′ are different.

The concentrations of complexes of dimethylanthracene in solutions of maleic anhydride (M) and citraconic anhydride (C) are related to the equilibrium constants for complex formation by equations 10 and 11. In a solution containing these reactants the adduct, P_M, of the diene and maleic anhydride forms rapidly by a process which may be represented by equation 12. This is accompanied by a much slower reaction 13 leading to the formation of a citraconic anhydride adduct, P_C.

$$K_M = (\text{ArH}\cdot\text{M})/(\text{ArH})(\text{M}) \qquad (10)$$

$$K_C = (\text{ArH}\cdot\text{C})/(\text{ArH})(\text{C}) \qquad (11)$$

$$\text{ArH} + \text{M} \xrightarrow{k_{1M}} P_M \qquad (12)$$

$$\text{ArH} + \text{C} \xrightarrow{k_{1C}} P_C \qquad (13)$$

For a series of rate runs in which both citraconic anhydride and maleic anhydride are present in large excess over the dimethylanthracene, rate constants k^* for the disappearance of dimethylanthracene may be evaluated from colorimetric rate measurements by using equation 1 with $k = k^*$ and (D) = (M). It can be shown that if equations 12 and 13 account uniquely for the disappearance of dimethylanthracene, k^* must be related to K_M, K_C, k_{1M} and k_{1C} by equation 14

$$\frac{k^*[1 + K_M(\text{M})] - k_{1M}}{(\text{C})} = \frac{k_{1C}}{(\text{M})} - k^*K_C \qquad (14)$$

Then for a series of runs of varying concentration of (C), values of the left-hand term of equation 14 when plotted *vs.* k^* should conform to a straight line of slope K_C and intercept $k_{1C}/(\text{M})$. In Fig. 2 the results of the several runs listed in Table V have been treated according to this equation. The ordinates of the various points which are shown are based on the K_M value reported in Table II. The ordinate intercept (marked by a cross) was calculated using equation 7, and the k and K_C values for citraconic anhydride and dimethylanthracene (Tables I and II). The line which is drawn was arbitrarily assigned a slope of 0.37 (based on the K_C value of Table II).

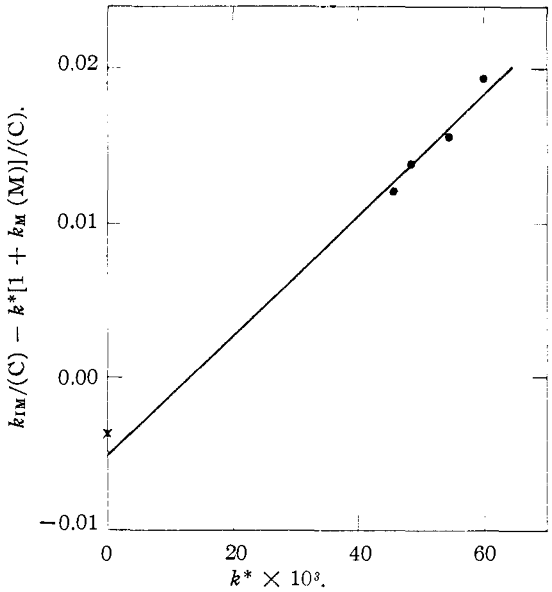

Fig. 2.—The variation in k^* for the dimethylanthracene–maleic anhydride reaction in the presence of varying amounts of citraconic anhydride (chloroform, 25.2°).

TABLE V

EFFECT OF CITRACONIC ANHYDRIDE (C) ON THE SECOND-ORDER RATE CONSTANTS FOR THE REACTION OF MALEIC ANHYDRIDE (M) AND DIMETHYLANTHRACENE IN $CHCl_3$ SOLUTION AT 25.2°

(M), mole/l.	$[(\text{ArH})_T]_i$, mole/l. × 10^3	(C), mole/l.	$10^3\,k^*$, mole^{-1} l. sec.$^{-1}$
0.0200	1.00	0	69.5
.0200	1.00	0.518	60.0
.0200	1.00	1.00	54.5
.0200	1.00	1.57	48.4
.0200	1.00	2.04	45.4

Experimental

The Dienes and Dienophiles.—9,10-Dimethylanthracene was prepared from anthraquinone by the method of Phillips and Cason.[16] The product, after fractional crystallization from benzene, melted from 179–182°. The anthracene used in these experiments was purified according to the directions of Kofahl and Lucas.[17]

Samples of maleic anhydride and of chloromaleic anhydride (Eastman Kodak Co. Organic Chemicals) were purified, respectively, by repeated recrystallization from chloroform (m.p. 51–53°) and by fractionation under reduced pressure (b.p. 147° (182 mm.)). The observed neutral equivalent of the chloromaleic anhydride was 67.0 as compared to a theoretical value of 66.3 for C_4HClO_3. Citraconic anhydride of b.p. 132° (74 mm.) and $n^{20}\text{D}$ 1.4710 was prepared from citric acid.[18]

The Solvents.—Eastman Kodak Co. Organic Chemicals spectroscopic grade chloroform was used without further purification except in the kinetic studies of the slow reaction of chloromaleic anhydride with anthracene and in the measurements of the equilibrium constant for complex formation between these two substances. The commercial chloroform was washed successively with sulfuric acid, water and sodium hydroxide solution, dried and distilled before use in these two sets of experiments. This precaution was necessary since chloromaleic anhydride undergoes slow reaction with the ethanol used to stabilize the chloroform. In the other reactions which were studied, essentially the same results were obtained whether or not the chloroform was treated to remove the stabilizer.

Eastman Kodak Co. Organic Chemicals sulfur-free carbon tetrachloride, Baker and Adamson glacial acetic acid and Baker Analyzed Reagent acetone were used without further purification.

The Rate Runs.—Weighed samples of the diene and dienophile were diluted to known volumes with the appropriate solvent (which had previously been adjusted to the temperature at which the run was to be made). Aliquots of these solutions were mixed to provide rate samples in which the dienophile concentration was in large excess over that of the diene. These samples were transferred immediately to 1 cm. absorption cells which were placed in the housing of a Beckman model DU spectrophotometer. The housing temperature was controlled by methods described previously.[19] The change in optical density of the solution as a function of time at some wave length between 400 and 450

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(16) D. D. Phillips and J. Cason, THIS JOURNAL, **74**, 2934 (1952).

(17) R. E. Kofahl and H. J. Lucas, *ibid.*, **76**, 3931 (1954).

(18) R. L. Shriner, S. G. Ford and L. J. Roll, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, pp. 140 and 368.

(19) R. M. Keefer and L. J. Andrews, THIS JOURNAL, **77**, 2164 (1955).

mμ was then measured against the solvent as a blank. The wave length was chosen in most cases to provide an initial optical density reading in the neighborhood of 1.0. Runs were followed to at least two-thirds of completion. At least eight optical density readings, including one at infinite time, were recorded during each run. Rate constants, k, were evaluated from the slopes of the straight lines obtained by plotting log d values *vs.* t (see equation 1). At least ten minutes time was allowed for equilibration of the sample to cell housing temperature in runs in the 2 and 45° region, and zero time was then recorded as the time of the first optical density measurements. In the case of very fast runs at 25.2° timing was accomplished with a battery of stopwatches. In fast runs, in which it was necessary to establish the time of mixing diene and dienophile solutions with reference to the time of the first optical density reading, the two solutions were mixed by dropping a small beaker containing one into a larger beaker containing the other.

The optical densities measured at infinite time in these runs were always small and were presumed to result from traces of impurities in the reaction mixtures. These final readings were subtracted from individual readings taken during the runs to provide the values of d_0 used in calculating rate constants by equation 1. The measured values of d_c included the absorption of both free and complexed diene. Within any one run in which the molar concentration of dienophile, (D), remained constant, d_c was related to the total concentration of both free and complexed diene, $(\mathrm{ArH})_\mathrm{T}$, by the expression

$$d_c = (\mathrm{ArH})_\mathrm{T}[\epsilon_{\mathrm{ArH}} + (\mathrm{D})K_1\epsilon_{\mathrm{ArH \cdot D}}]/[1 + K_1(\mathrm{D})] \quad (15)$$

In this equation ϵ_{ArH} and $\epsilon_{\mathrm{ArH \cdot D}}$ are the extinction coefficients of free and complexed diene, and K_1 is the equilibrium constant for formation of the complex. In some runs on dimethylanthracene and maleic anhydride the reaction rate was followed at one wave length until the diene concentration was a small fraction of its initial value. Then the wave length setting of the spectrophotometer was shifted downward to a region of more intense diene absorption and a new series of optical density measurements were made. Rate constants calculated from these two sets of data by equation 1 were always in excellent agreement with each other.

The Equilibrium Constant for Complex Formation.—A series of four or five solutions were prepared in which the dienophile concentration ranged from about 1.5–0 3 M and the diene concentrations were of the order of magnitude of 10^{-2}–10^{-3} M. The optical densities of these solutions *vs.* the solvent as blank were measured in 1 cm. absorption cells over a series of wave lengths in the 400–450 mμ region. In all cases the cell housing temperature was controlled to within 0.1° during the course of the measurements.

In solutions of dimethylanthracene and maleic anhydride Diels–Alder reaction occurred too rapidly to permit direct measurement of the optical densities of the freshly prepared solution. These were conveniently calculated by following the rates of the Diels–Alder reactions in these solutions at 450 mμ and extrapolating plots of log d_t *vs.* time back to the times of mixing.

The equilibrium constants, K_1, for complex formation were calculated by graphical analysis of the data according to the equation[20]

$$1/(\epsilon_a - \epsilon_\mathrm{D}) = 1/K_1(\mathrm{D})\,(\epsilon_{\mathrm{ArH \cdot D}} - \epsilon_\mathrm{D}) + 1/(\epsilon_{\mathrm{ArH \cdot D}} - \epsilon_\mathrm{D}) \quad (16)$$

in which $\epsilon_a = d/(\mathrm{ArH})_\mathrm{T}$. Values of ϵ_D obtained from separate measurements of diene-free solutions were generally small or zero over the wave length ranges of these investigations.

The Diels–Alder Adducts.—Product isolation experiments were designed to check the identity of two of the Diels–Alder adducts (A and B) formed under reaction conditions which were comparable to those used in the kinetic work.

(A) **9,10-Dimethyl-9,10-dihydroanthracene-9,10-endo-α,β-succinic Anhydride.**—A solution of 0.300 g. (0.00145 mole) of dimethylanthracene and 0.144 g. (0.00147 mole) of maleic anhydride in 10 cc. of chloroform was prepared at room temperature. Crystals began to precipitate from the deep orange solution almost immediately, and the solution rapidly became lighter in color. After one hour the white crystals (0.37 g.) were filtered. After recrystallization from ethyl acetate the product melted[8] from 331–333°.

(B) **9,10-Dimethyl-9,10-dihydroanthracene-9,10-endo-α-chloro-α,β-succinic Anhydride.**—A solution of 0.645 g. (0.00312 mole) of dimethylanthracene and 0.440 g. (0.00332 mole) of chloromaleic anhydride in 10 cc. of chloroform was allowed to stand overnight during which time its color changed from deep red to light yellow. The solvent was evaporated under reduced pressure, and the crystalline residue was triturated with ether to remove a yellow colored contaminant. The remaining white powder (0.54 g.) was recrystallized twice from aqueous acetic acid to yield the chlorine containing anhydride in the form of fine white needles of m.p. 173–175°.

Anal. Calcd. for $C_{20}H_{15}O_3Cl$: C, 70.90; H, 4.46. Found: C, 71.03; H, 4.53.

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(20) J. A. A. Ketelaar, C. van de Stolpe, A. Goudsmit and W. Dzcubas, *Rec. trav. chim.*, **71**, 1104 (1952).

DAVIS, CALIFORNIA

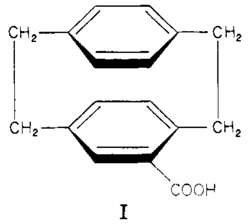
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Macro Rings. XII. Stereochemical Consequences of Steric Compression in the Smallest Paracyclophane[1]

BY DONALD J. CRAM AND NORMAN L. ALLINGER

RECEIVED JUNE 28, 1955

The preparation, proof of structure and complete resolution of compound I is described, as well as the anomalous behavior of the parent hydrocarbon (II, $n = m = 2$) upon catalytic hydrogenation.



I

The preparation, properties and some reactions of the paracyclophanes II in which n and m have been varied from 2 to 6 have been described in previous publications.[2] When the value of either n or m became smaller than 4, the spectral properties of the compounds became abnormal, the departures from normality increasing as the two benzene rings

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(2) Paper XI in this series, D. J. Cram and M. Cordon, THIS JOURNAL, **77**, 4090 (1955).