Nature of the Transition State in Some Diels–Alder Reactions[1]

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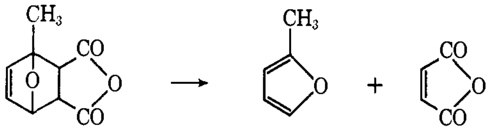
Abstract: The rates of Diels–Alder reactions of maleic anhydride in diethyl succinate with anthracene, and its monobenzo and dibenzo derivatives, have been measured; analysis of the results, using SCF–MO theory, indicates that the reaction involves an essentially symmetric, cyclic, transition state. A comparison of the rates of retion of isoprene with ethylene, acrolein, and maleic anhydride indicates that the transition state for the acrolein reaction, if cyclic, is unsymmetrical. Arrhenius parameters are reported for the reaction of isoprene with maleic anhydride in a number of solvents.

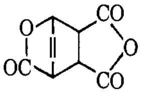
While the available evidence seems to support a one-step mechanism for the Diels–Alder reaction, involving a cyclic "aromatic" transition state of the type first proposed some time ago by Evans,[3] alternative two-step mechanisms involving intermediate diradicals (or even perhaps in some cases zwitterions) have not yet been definitely excluded.[4]

If the reaction does take place by the one-step mechanism, there is still a further uncertainty concerning the symmetry of the transition state. This can either be symmetrical, the two new bonds being formed in it to equal extents, or unsymmetrical, one of the new bonds being much stronger than the other.[5]

These distinctions are typical of a class of mechanistic problems that involve the detailed timing of bond-forming and bond-breaking processes in chemical reactions, and the situation in the Diels–Alder reaction is also typical in being very difficult to investigate experimentally. Almost the only convincing line of approach so far followed in this connection has involved the use of secondary isotope effects, and studies of this kind have led to conflicting conclusions. Thus Seltzer[6] concluded from a study of secondary deuterium isotope effects on the reverse Diels–Alder reaction of I to (II + III) that the transition state must be symmetrical; the same would of course be true for the reverse reaction, *i.e.*, the Diels–Alder association of II and III to give I. On the other hand, Goldstein and Thayer[7] have concluded from a similar study of ^{13}C and ^{18}O isotope effects on the rate of the dissociation of IV to V and carbon dioxide that the transition state must be highly unsymmetrical; although the dissociation of IV is not strictly a reverse Diels–Alder reaction, it is clearly analogous to one.



I II III



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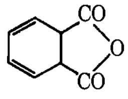
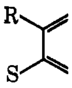


V

Another approach has been used by Charton[8] based in effect on the following argument. Consider the reaction of a butadiene (VI), where R and S may be hydrogen or substituents, with a symmetrical dienophile. If the transition state is symmetrical, the positions occupied by R and S are equivalent, so the rate for a disubstituted diene, relative to butadiene, should be given by $K_R K_S$, where K_R and K_S are the ratios of rates of the corresponding monosubstituted butadienes to butadiene. If, however, the transition state is unsymmetrical, so that the positions occupied by R and S in VI are not equivalent, then this additivity of substituent effects should not hold. Similar considerations should apply to the reactions of a symmetrical diene with the dienophiles VII and VIII, and to the reactions of the anthracene derivatives IX with a symmetrical dienophile.



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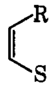

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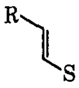

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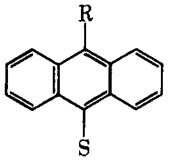

IX

Charton analyzed rate data taken from the literature for a large number of Diels–Alder reactions in terms of the Hammett relation and concluded on this basis that such additivity holds for all four of these systems, though with less certainty for IX. Careful examination shows, however, that these conclusions do not follow from the data quoted by him and are probably consequences of the unsatisfactory method of analysis he adopted.

In order to establish additivity, it is essential to have rate data for the unsubstituted case (R = S = H), and for the monosubstituted case for each substituent X (*i.e.*, R = X; S = H), because the transition state for the unsymmetrical monosubstituted reactant is likely to be less symmetrical than that for the unsubstituted case, or for the disubstituted case. Complete series of data are in fact available only for the reactions of maleic anhydride with VI (R and S being H, CH_3, or

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[2] Robert A. Welch Postdoctoral Fellow; Department of Chemistry, Furman University, Greenville, S. C. 29613.

[3] M. G. Evans, *Trans. Faraday Soc.*, **35**, 824 (1939).

[4] See, *e.g.*, J. A. Berson and A. Remanick, *J. Am. Chem. Soc.*, **83**, 4947 (1961); R. P. Lutz and J. D. Roberts, *ibid.*, **83**, 2198 (1961). D. E. Van Sickle and J. O. Rodin, *ibid.*, **86**, 3091 (1964).

[5] See R. B. Woodward and T. Katz, *Tetrahedron*, **5**, 70 (1959).

[6] S. Seltzer, *J. Am. Chem. Soc.*, **87**, 1534 (1965).

[7] M. J. Goldstein and G. L. Thayer, Jr., *ibid.*, **87**, 1933 (1965).

[8] M. Charton, *J. Org. Chem.*, **31**, 3745 (1966).

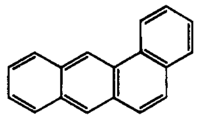
Cl) and with VIII (R and S being H, CH_3, C_2H_5, Cl, or OCH_3) and in both these series there are significant deviations from additivity. These are obscured by the method of analysis adopted because the deviations are numerically small; they are nevertheless significant because the overall effects of the substituents on the rate are also small.

In the case of the dienophiles VII and VIII, this simple analysis fails since no rate data are available for ethylene (*i.e.*, R = S = H). Indeed, the only monosubstituted ethylenes for which data are available are acrylonitrile and methyl acrylate—and these react at very similar rates. Even so, one can see at once from the results quoted by Charton that additivity does not hold. Thus whereas acrylonitrile reacts at almost the same rate as methyl acrylate with cyclopentadiene, it reacts twice as fast as methyl acrylate with 9,10-dimethylanthracene and the ratios of rates for maleonitrile and dimethyl maleate are very large (100 for cyclopentadiene and 2000 for 9,10-dimethylanthracene). Likewise the rates of reaction of dimethylanthracene with dimethyl fumarate, methyl *trans*-β-cyanoacrylate, and fumaronitrile are in the ratio 1:4.1:21.

Some of these deviations may of course be due to steric effects, as Charton points out; however in that case it is not easy to see how any reliance can be placed on his analysis, given that steric effects are not taken into account in the Hammett equation and given that such effects are undoubtedly present in many of the key compounds. In any case the evidence presented later in this paper shows that his conclusions are almost certainly incorrect.

Some years ago one of us suggested[9] that information might be obtained concerning the mechanisms of reactions by comparing the patterns of rates predicted by MO theory for a series of suitable reactants with various possible assumed structures for the transition state. In order to make the best use of this approach, it was pointed out that the compounds should, if possible, be corresponding derivatives of a series of alternant hydrocarbons, for since the carbon atoms in alternant hydrocarbons are neutral, the relative rates in such a series will be determined solely by differences in resonance interactions, which are easy to calculate, not by inductive or field effects. Although this procedure was applied very successfully to aromatic substitution,[10] and to nucleophilic aliphatic substitution,[11] and although it has obvious advantages over the conventional technique of using substituted benzenes and applying the Hammett relation, surprisingly few other applications have as yet been reported.[12] The main purpose of the present investigation was to apply this technique to the Diels–Alder reaction.

In order to do this, we need a series of alternant hydrocarbons as reactants in which the relative rates of reaction would be expected to depend on the symmetry of the transition state. Such a series is provided by anthracene (IX, R = S = H), the two monobenzanthracenes X and XI, and the three dibenzanthracenes XII, XIII, XIV. If the reaction takes place in two steps *via* an intermediate biradical XV, the formation of XV being the slow step, one would expect the rates to run parallel to the localization energies at the most reactive individual positions in the hydrocarbons, for the formation of XV is in effect an aromatic substitution reaction and the rates of such reactions are known to correlate well with localization energies.[13] If on the other hand the reaction is concerted and takes place *via* the symmetrical transition state XVI, one would expect the rate to run parallel to the energy required to remove the two relevant carbon atoms from the diene, *i.e.*, the paralocalization energy of Brown.[14] Finally, if the reaction is concerted but takes place *via* an unsymmetrical transition state, one would expect the rates to show an intermediate dependence.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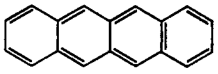
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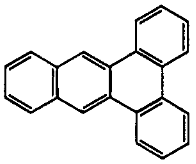
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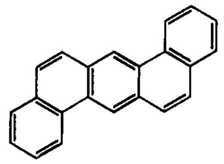
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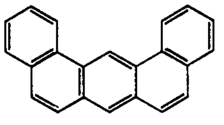
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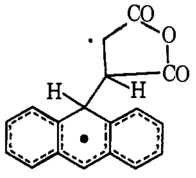

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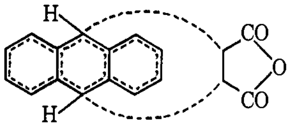

XVI

In his original papers, Brown[14] showed that the qualitative data then available concerning the ease with which various aromatic hydrocarbons underwent Diels–Alder reactions ran parallel to paralocalization energies calculated by the HMO method. His object, however, was to test the HMO method in a possibly new connection rather than use it to establish mechanisms; otherwise he would undoubtedly have pointed out that the data available to him could equally well have been explained in terms of the two-step mechanism since there is a qualitative parallel between paralocalization energies in aromatic hydrocarbons and localization energies of the more reactive of the two positions in question.

Quantitatively, however, there are marked divergences between the two quantities, in particular for the series of compounds IX–XIV. A comparison of the rates of their Diels–Alder reactions with a given dienophile with localization and paralocalization en-

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(9) See M. J. S. Dewar, *Advan. Chem. Phys.*, **8**, 65 (1964), and papers cited there.

(10) M. J. S. Dewar, T. Mole, and E. W. T. Warford, *J. Chem. Soc.*, 3581 (1956).

(11) M. J. S. Dewar and R. J. Sampson, *ibid.*, 2946 (1957).

(12) For a recent example, see M. D. Bentley and M. J. S. Dewar, *J. Am. Chem. Soc.*, **90**, 1075 (1968).

(13) See M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1969.

(14) R. D. Brown, *J. Chem. Soc.*, 691, 2730 (1950); 1612, 3129 (1951).

ergies should therefore allow a distinction to be drawn between the various mechanistic possibilities. Since no such rate data were available, we decided to provide them.

A second investigation, which was carried out some years ago,[15] followed the principles indicated above in the discussion of the work of Charton.[8] The object was to measure the rates of reaction of a given diene with ethylene, a monosubstituted ethylene $CH_2{=}CHX$, and a disubstituted ethylene $XCH{=}CHX$, in order to see if the effects of the two substituent groups X in the latter were additive.

Finally, we are taking this opportunity to report the results of a detailed study of substituent effects on the rate of the reaction between isoprene and maleic anhydride; although the conclusions reached are now familiar, no such detailed study has as yet been reported and the work has aroused interest among theoreticians concerned with the theory of solvent effects.

Experimental Section

The reagents and solvents were pure commercial samples and were recrystallized or distilled before use. Their physical properties agreed with those reported in the literature.

The Diels–Alder reactions of maleic anhydride with IX–XIV are well known; we checked that the reactions took place cleanly under our conditions, giving the products reported previously. After various trials, we standardized on diethyl succinate as solvent; this has the advantage of being relatively nonvolatile and of minimizing side reactions that can give colored by-products.

The reactions of isoprene with maleic anhydride[16] and with acrolein[17] have also been reported; both appeared to take place cleanly under the conditions we used. The reproducibility of the results implied very strongly that radical side reactions were not interfering to any significant extent.

The reactions were carried out by batch methods in glass ampoules sealed under vacuum. In the case of the isoprene–acrolein reaction, 0.5% of hydroquinone was added as an inhibitor. Varying the amount of hydroquinone had no effect on the rate, provided enough was added to inhibit polymerization.

Analytical Procedures. A. Anthracene Reactions. The reactions of IX–XIV were followed spectrophotometrically, using a Beckman DK2 spectrophotometer to determine the amount of unreacted hydrocarbon in each ampoule from the absorption at the long wave maximum for the hydrocarbon (*ca.* 390 nm for IX and X, 350 nm for XII–XIV, 480 nm for XI).

B. Isoprene–Maleic Anhydride Reactions. The reactions of maleic anhydride with isoprene in solvents other than nitrobenzene were followed by colorimetric estimation of maleic anhydride, making use of the deep orange complex it forms with dimethylaniline. A sample (1 ml) of the solution was added to a dry solution of dimethylaniline in benzene (20 ml of 10% v/v) and the color measured with a Hilger Spekker photometer, using a violet (λ 405 nm) filter. The concentrations were determined from the absorptions by means of an empirical correction curve; it was established that the calibration was not affected by the presence of a small amount (5%) of the solvent used in the Diels–Alder reaction.

The procedure could not be used for reactions carried out in nitrobenzene, since nitrobenzene itself forms a colored complex with dimethylaniline. However, maleic acid is a much stronger acid (pK = 1.83) than succinic acid (pK = 4.18), and the Diels–Alder adduct is a derivative of *succinic acid*; consequently it was found possible to estimate unchanged maleic acid in presence of the adduct by potentiometric titration. The solution (3 ml) was shaken vigorously for 1 min with a mixture of 0.1 *N* potassium hydroxide solution (10 ml) and ether (10 ml). The aqueous layer was separated and the ether layer washed with water (5 ml). The combined water layers were titrated with 0.1 *N* hydrochloric acid to pH 3.50. Under these conditions maleic acid titrates as a monobasic acid and neither succinic acid nor the Diels–Alder adduct interferes. A correction was necessary in view of the low pH at the end point; this was found by a blank titration, using pure solvent.

C. Acrolein Reactions. Acrolein, unlike isoprene or the Diels–Alder product, absorbs strongly at 3650 Å; it could therefore be estimated spectrophotometrically.

Correction for Thermal Expansion. In all cases the concentrations of reactants were corrected for thermal expansion of the solvent using values for the densities of the solvents recorded in Beilstein or Landolt-Bernstein.

Order of Reactions. A. Maleic Anhydride–Isoprene Reaction. The reaction in benzene was shown to be accurately of second order by varying the concentrations of the reactants at two temperatures (Table I). Each value for the rate constant is the mean of concordant measurements from at least two different runs. The individual runs in all solvents followed second-order kinetics throughout within the limits of experimental error in the analyses.

Table I. Order of the Isoprene–Maleic Anhydride Reaction in Benzene

Temp, °C	Initial molar concn Maleic anhydride	 Isoprene	10^5(rate constant), l. mole^{-1} sec^{-1}
30.3	0.1	0.1	1.75
30.3	0.25	0.25	1.72
30.3	0.5	0.25	1.78
30.3	0.5	0.5	1.75
60.3	0.1	0.1	10.4
60.3	0.25	0.25	10.5
60.3	0.5	0.5	10.0

B. Acrolein Reactions. The individual runs again followed second-order kinetics accurately, and the second-order rate constants in anisole were unaffected by the inital concentrations of reactants (Table II).

Table II. Order of the Isoprene–Acrolein Reaction in Anisole at 60.3°

Initial molar concentration Isoprene	 Acrolein	10^5(rate constant), l. mol^{-1} sec^{-1}
0.5	1.0	1.68
0.5	0.5	1.71
0.2	0.5	1.73

C. Anthracene Reactions. The reactions with maleic anhydride followed second-order kinetics; in each case the order was confirmed by carrying out reactions with different initial concentrations of maleic anhydride.

Determination of Rate Constants. The reactions of isoprene with maleic anhydride or acrolein are simple, irreversible, second-order reactions and the rate constants were found by standard graphical methods. The individual rate constants were always reproducible to ±2%; thus five measurements for the reaction between maleic anhydride and isoprene in benzene at 30.3° (initial concentration of each reactant, 0.5 *M*) gave the following values for the rate constant ($\times 10^{-4}$ mole l.$^{-1}$ sec^{-1}): 1.73, 1.77, 1.75, 1.78, 1.74. Arrhenius plots (see below) indicated that the errors in the rate constants did not exceed 5%.

The reactions of IX, X, XI, and XII with maleic anhydride in diethyl succinate were followed by using a large excess of maleic anhydride, the concentrations of maleic anhydride and hydrocarbon being *ca.* 0.1 and *ca.* 0.0025 *M*, respectively, so that the reaction initially followed first-order kinetics. The second-order rate constant (k_1) was found by dividing the pseudo-first-order rate constant by the concentration of maleic anhydride.

The reactions of XIII and XIV presented difficulties, being somewhat irreproducible and giving curved first-order plots. These reactions are reversible, and it was found that the reverse reactions of the Diels–Alder adducts XVII and XVIII to XIII and XIV gave reproducible rates; *viz.* (MA = maleic anhydride)

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(15) A preliminary account of this work has appeared but contained an error which is corrected here: M. J. S. Dewar, *Tetrahedron Lett.*, **4**, 16 (1959).

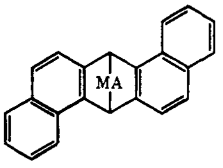
(16) See N. Rabjohn, M. F. Drumm, and R. L. Elliot, *J. Am. Chem. Soc.*, **78**, 1631 (1956).

(17) See E. F. Lutz and G. M. Bailey, *ibid.*, **86**, 3899 (1964).

Table III. Diels-Alder Rate Constants for Reactions with Maleic Anhydride[a]

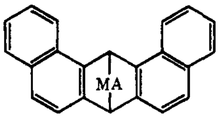
Dienes	$k_1 \times 10^4$,[b] l. mole^{-1} sec^{-1}	Electrophilic localization energy,[c] eV	Paralocalization energy,[d] eV
Anthracene (IX, R = S = H)	75.5	−1.681	(0)
Benz[*a*]anthracene (X)	6.92	−1.684	0.237
Naphthacene (XI)	1380[e,f]	−2.073	−0.232
Dibenz[*a*,*c*]anthracene (XII)	3.58	−1.593	0.395
Dibenz[*a*,*h*]anthracene (XIII)	0.747[g]	−1.594	0.440
Dibenz[*a*,*j*]anthracene (XIV)	0.675[h]	−1.659	0.440

[a] In diethyl succinate at 129.7 ± 0.1°. [b] Duplicate runs indicate an average deviation of ±5% or less. [c] Relative to benzene. [d] Relative to anthracene. [e] Extrapolated from data at 15.7 and 39.7° ($k_1 \times 10^4$ = 3.38 and 20.8 l./mole sec, respectively). [f] Corrected for two equivalent reaction sites. [g] Evaluated from K_{DA} = 5.81 and $k_2 = 0.135 \times 10^{-4}$ sec^{-1}. [h] Evaluated from K_{DA} = 5.98 and $k_2 = 0.113 \times 10^{-4}$ sec^{-1}.



$\xrightarrow{k_2}$ XIII + MA

XVII



$\xrightarrow{k_2}$ XIV + MA

XVIII

Reproducible equilibrium constants could also be obtained without difficulty for both these reactions. The rates of the Diels-Alder reactions of XIII and XIV with MA were therefore obtained by dividing the equilibrium constants (k_{DA}) by the rate constants (k_2) for the reverse reactions.

The rate constants for the reactions of IX-XIV with MA were less than those for the reactions of isoprene; however, in most cases they are believed to be reliable to ±5%.

The rates of reaction of naphthacene (XI) were so much greater than those for the other hydrocarbons that the rate constant could not be measured at the same temperature (130°); the rates were therefore measured at 15 and 40°, and the rate constant at 130° deduced by extrapolation, using the Arrhenius equation. This value is obviously less reliable than those measured directly.

Results and Discussion

The rate constants estimated for the reactions of maleic anhydride with anthracene and its benzo derivatives are listed in Table III.

Ideally one would like to compare the observed pattern of rates with those predicted theoretically for the one-step and two-step mechanisms, by calculating the energies of the corresponding transition states, XV and XVI; unfortunately meaningful calculations of this kind are not possible at present. We therefore followed the usual procedure[9] of assuming linear relations between energies of reaction and of activation, in which case there should be a linear relation between the logarithm of the rate and the calculated energy of reaction.[18] In the two-step reaction, the rate-determining step involves the production of an arenonium intermediate; the rate of such a process should run parallel to the rate of a typical aromatic substitution reaction and so be related to the localization energy, *i.e.*, the relative difference in energy between the parent hydrocarbon and the intermediate. The one-step mechanism should lead directly to the Diels-Alder adduct: here the rate should be related to the difference in energy between the parent hydrocarbon and the adduct in which two *para* carbon atoms have become saturated, *i.e.*, the paralocalization energy.[14]

Earlier studies of reactivity were based on the HMO or PMO methods; however, a superior procedure has recently been developed here,[19] based on the use of a semiempirical SCF-MO approach. In cases where suitable experimental data are available, *e.g.*, aromatic substitution[10] or nucleophilic aliphatic substitution, the results are in much better agreement with experiment than those given by earlier and cruder treatments.[13] The last two columns of Table III show the relevant localization and paralocalization energies, in electron volts relative to benzene, calculated by the latest version[19] of this treatment. The localization energies are in fact for electrophilic substitution; however, it is known[13,19] that in the case of alternant hydrocarbons there is an almost exact parallel between electrophilic and radical localization energies.

Figure 1 shows plots of log k_1 against the relative localization and paralocalization energies listed in Table III. There is virtually no correlation in the first case, whereas in the second the points all lie close to a straight line. As the arguments given earlier indicate, this result implies very strongly indeed that the transition state has a cyclic structure. The two-step mechanism seems to be definitely excluded; indeed, it seems almost certain that the transition state must be not only cyclic but also essentially symmetric, in agreement with the conclusions of Seltzer[6] for the analogous reaction of 2-methylfuran with maleic anhydride.

A second criterion of the Diels-Alder transition state should be provided, as indicated in the introduction, by comparison of the rates of reaction of a given diene with ethylene, with a monosubstituted ethylene $CH_2{=}CHR$, and a disubstituted ethylene $RCH{=}CHR$. The choice of diene is dictated by the fact that the only Diels-Alder reaction of ethylene whose rate has been accurately measured is that with butadiene.[20] Rowley and Steiner[20] measured this at high temperatures in the gas phase, but their measurements covered so wide a range of temperature, and led to so good an Arrhenius plot, that the rates can be safely extrapolated to temperatures where the rates for other dienophiles can be conveniently measured. Since the rates

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(18) This of course also rests on the usual assumption that the relative rates of reaction of a related series of compounds can be calculated assuming a constant entropy of activation; see ref 9.

(19) M. J. S. Dewar and Carlos de Llano, *J. Am. Chem. Soc.*, 91, 789 (1969); M. J. S. Dewar and Toshifumi Morita, *ibid.*, 91, 796 (1969); papers cited there.

(20) D. Rowley and H. Steiner, *Discussions Faraday Soc.*, 10, 198 (1951).

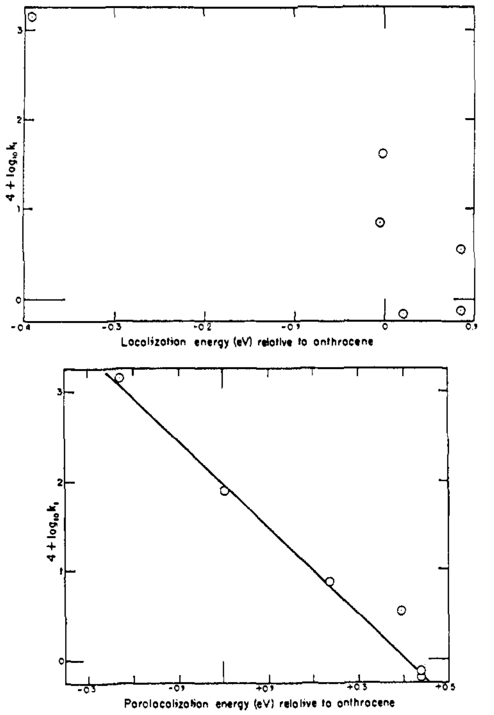

Figure 1. Plots of log k_1 for the reactions of IX–XIV with maleic anhydride *vs.* (a) localization energies for the most reactive positions; (b) paralocalizaton energies for the most reactive pairs of positions.

of Diels–Alder reactions between hydrocarbons are known[21] to be the same in solution as in the gas phase, the extrapolated rates for ethylene can be compared with rates for other dienophiles in solution. It can also be assumed that the rates of reaction of butadiene and isoprene with a nonpolar dienophile, *i.e.*, ethylene, will be the same since the rates of their reactions with the polar dienophile, acrolein, are almost identical;[22] since isoprene is easier to handle than butadiene, we decided to use it as our diene.

For R, we need a strongly activating group (to give the maximum spread in rates) which is not subject to steric hindrance; nitrile would be the obvious choice, but at the time this work was carried out, maleonitrile and fumaronitrile were not accessible. The best choice seemed to be anhydride, maleic anhydride serving perfectly as the disubstituted ethylene. The corresponding monosubstituted diene should have been acrylic anhydride, which, however, was also somewhat inaccessible; since the carbonyl in an anhydride group should be more active than that in an ester, acrolein (*i.e.*, R = CHO) seemed the best substitute.

Table IV shows rate constants for the reactions of acrolein and maleic anhydride with isoprene in anisole at 100.3°, together with a value for the corresponding reaction of ethylene estimated as indicated above for the results of Rowley and Steiner.[20] The last two columns of Table IV show the relative rates of the three reactions.

It will be seen that the ratio of rates for the reactions of acrolein and ethylene (61,000) is enormously greater than that (71) for maleic anhydride and acrolein. The difference is too great by orders of magnitude to be attributed to errors in the estimated value for the ethylene reaction, or to differences between the electronic effects of the carbonyl groups in acrolein and maleic anhydride.[23] These results therefore seem to indicate very strongly indeed that the transition state for the isoprene–acrolein reaction cannot have a symmetrical cyclic structure. They do not distinguish between a two-step mechanism involving an intermediate biradical (*cf.* XV) and a one-step mechanism involving a cyclic but unsymmetrical transition state. However, it seems very likely that the transition state is in fact still cyclic because the Arrhenius parameters for the Diels–Alder reactions of dienophiles of the type $CH_2{=}CHX$ and $XCH{=}CHX$ are similar, implying similar steric restraints in the transition state.[25]

Table IV. Second-Order Rate Constants (k) for Diels–Alder Reactions of Isoprene in Anisole at 100.3°

Dienophile	k, l. mole^{-1} sec^{-1}	k(rel)
Ethylene[a]	3.0×10^{-9}	1/61,000
Acrolein	1.82×10^{-4}	1
Maleic anhydride	1.28×10^{-2}	71

[a] See text.

The results reported here are also consistent with those of Sauer, *et al.*,[25] in implying a relatively small difference in rate between mono- and disubstituted ethylenes as dienophiles; they found the relative rates of reaction of cyclopentadiene with acrylonitrile, maleonitrile, and fumaronitrile in dioxane at 20° to be 1:77.9:88.5. Unfortunately there are no measurements or estimates of the rate of the ethylene–cyclopentadiene reaction under these conditions, or for the rates of reaction of butadiene or isoprene with the cyanoethylenes. According to our results, the small difference in rate between mono- and disubstituted ethylenes as dienophiles is due to the asymmetry of the transition state for the Diels–Alder reaction of highly unsymmetrical dienophiles (*cf.* Goldstein and Thayer[7]), the single substituent exerting a greater effect than either of two equivalent ones in a symmetrical disubstituted dienophile $XCH{=}CHX$.

A final investigation was concerned with the effect of solvent on the rate of the Diels–Alder reaction. At the time this work was carried out, only one study of solvent effects had been reported,[26] for the reaction of cyclopentadiene with *p*-benzoquinone. Only four solvents were studied and the Arrhenius *A* factor for these varied over a range of 100:1. Table V shows the results of a detailed study of the isoprene–maleic anhydride reaction in a wide range of solvents.

The results in Table V agree with some other recent studies[27] in indicating that the rate of the reaction varies little with the solvent; the total range of rates is

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[21] A. Wasserman, *Trans. Faraday Soc.*, **34**, 128 (1938).

[22] G. B. Kistiakowsky and J. R. Lacher, *J. Am. Chem. Soc.*, **58**, 123 (1936).

[23] The difference must be less than that between the carbonyl groups in acrolein and methyl acrylate, since carbomethoxy is a less active group than carboxylic anhydride. The rates of reaction of cyclopentadiene, or of 2,3-dimethylbutadiene, with acrolein and with methyl acrylate differ by less than a factor of 3,[24] so the error due to using acrolein instead of acrylic anhydride must be less than this.

[24] A. I. Konovalov, *Dokl. Akad. Nauk SSSR*, 162, 343 (1965).

[25] J. Sauer, H. Wiest, and A. Mielert, *Chem. Ber.*, **97**, 3183 (1964).

[26] R. A. Fairclough and C. N. Hinshelwood, *J. Chem. Soc.*, 236 (1938).

[27] D. Long, Dissertation, Universität Munich, 1963; J. Sauer, Habilitation Thesis, Universität Munich, 1963; see J. Sauer, *Angew. Chem. Intern. Ed. Engl.*, 6, 16 (1967).

Table V. Rate Constants and Arrhenius Parameters for the Reaction between Maleic Anhydride and Isoprene

Solvent (dielectric constant)	10^5k_1, l. mole^{-1} sec^{-1} (temp, °C)^a 0	30.3	60.3	90.3	100.3	Arrhenius parameters, E kcal	10^5A l. mol^{-1}
Benzene (2.3)	1.62 (1.72)	17.5 (16.6)	104 (104)		762 (760)	12.3	1.20
Anisole (4.3)	2.59 (2.53)	25.2 (25.5)	166 (168)		1290 (1290)	12.6	3.07
Isopropyl ether (4.3)		5.01 (5.11)	43.8 (42.7)		411 (423)	14.2	8.70
Veratrole (4.5)		31.0 (31.2)	215 (208)	1010 (1010)		12.7	4.40
Chlorobenzene (5.6)	2.36 (2.36)	25.2 (23.9)	143 (157)		1220 (1200)	12.6	2.86
m-Dichlorobenzene (5.0)		33.0 (33.9)	230 (219)	992 (1040)		12.5	3.43
o-Dichlorobenzene (7.5)	7.62 (7.62)	66.7 (66.8)	367 (390)	1730 (1690)	2670 (2620)	11.8	2.12
Benzonitrile (26.5)	3.17 (3.17)	34.3 (34.6)	223 (241)	1225 (1220)		13.0	8.03
Nitrobenzene (36.1)	4.89 (4.89)	52.9 (47.0)	292 (295)		2220 (2150)	12.3	3.41
Nitromethane (39)	3.09 (3.20)	33.2 (30.8)	210 (193)		1330 (1410)	12.3	4.60

[a] Values in parentheses are calculated from the listed Arrhenius parameters. Initial concentration of each reactant was 0.5 *M*.

only about 10:1, and there is little correlation with the dielectric constant. Therefore although the reaction involves a rather polar dienophile, the transition state must be little more polar than the reactants. As one would expect on this basis the Arrhenius *A* factor varies little over the series; this makes the large variation reported by Fairclough and Hinshelwood[26] all the more puzzling. As yet, no other study of solvent effects as a function of temperature seems to have been reported.

The results listed in Table V may also be of interest in connection with the theory of solvent effects, representing as they do a set of accurate and consistent data for a homogeneous bimolecular reaction between neutral reagents, leading to neutral products, in a wide range of solvents.

The Photochemistry of Singlet and Triplet Azide Excited States[1a]

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Abstract: The direct and photosensitized chemistry of a series of 2-azidobiphenyls has been studied. Direct excitation of 10^{-2} *M* solutions of the azides results in predominate formation of carbazoles accompanied by lower yields of azo compounds. The azo compound formation is quenched by dienes, oxygen, and pyrene with a resultant increase in carbazole yields. When acetone, acetophenone, benzophenone, or *m*-methoxyacetophenone were used to sensitize the decomposition of the azide, azo compounds were obtained. The quantum yield for the disappearance of 2-azidobiphenyl in the acetophenone-sensitized irradiation was found to be about 0.30. In contrast, aromatic hydrocarbons such as triphenylene, naphthalene, and pyrene sensitize the 2-azidobiphenyl with involvement of their respective singlet states; this leads to predominate formation of carbazole. Pyrene has been utilized in a unique sense. It functions to populate the azide excited singlet state by singlet energy transfer and also serves as a quencher for the excited triplet azide.

The thermolyses[2] of aromatic and aliphatic azides have attracted considerable attention in recent years. In many of these studies the nitrene in either its singlet or triplet state has been accepted as the reactive intermediate. Likewise in the direct excitation of azides by uv light the nitrene has been implicated as an important intermediate.[3,4]

In contrast to the thermolysis and direct photolysis results, investigations on the sensitized decomposition of azides have produced no consistent picture.[3e,j-l,5b,c] Thus it has been proposed that a triplet azide and probably a nitrene were intermediates in the aromatic hydrocarbon sensitized decomposition of triarylmethyl azides,[3g] while acetophenone-sensitized decomposition of ethyl azidoformate did not afford a triplet nitrene.[3j] Furthermore, the photosensitized decomposition of

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(1) (a) Part IV in this series. For preliminary reports: J. S. Swenton, *Tetrahedron Lett.*, 3421 (1968); J. S. Swenton, T. J. Ikeler, B. H. Williams, *Chem. Commun.*, 1263 (1969); (b) Sinclair Oil Fellow, 1966; (c) undergraduate research participant.

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