Possible Role of Charge-Transfer Complexes in Cationic Polar Cycloaddition

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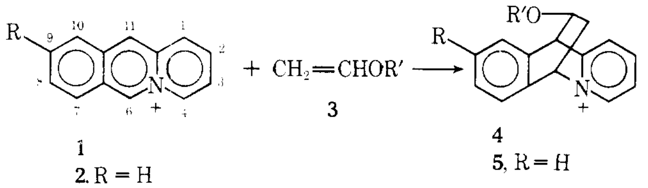
The log of the relative rate constants (k/k_0) for the cycloaddition of ethyl vinyl ether for a series of 9-substituted acridizinium perchlorates gave a significant correlation when plotted against the Hammett σ_p. The values for ρ were higher than those found earlier using styrene or acrylonitrile with the same substrate, but significantly lower than would be expected for a two-step reaction. The reaction in which para-substituted phenoxyethylenes are added to the acridizinium ion was studied in the same way, and a significant correlation between log k/k_0 and the σ_n of van Bekkum, Verkade, and Wepster was found. The activation parameters for the forward and retro reactions were determined for the cycloaddition of 2,3-dimethylisoquinolinium iodide with ethyl vinyl ether and found to be within the ranges established for the classical Diels–Alder reaction. A significant correlation has been found between the log of the relative rates of cycloaddition of para-substituted styrenes and published values for ^{13}C chemical shift of the β carbon of the styrenes. Spectroscopic evidence indicates that the acridizinium ion forms charge-transfer complexes with donor molecules, and analysis of the second-order rate constant for the cycloaddition of *N*-vinylcarbazole with the acridizinium ion shows that there is a decrease in the apparent rate constant with increased concentration of *N*-vinylcarbazole. These data can be interpreted as evidence for the presence of a charge-transfer complex in the reaction mixture. It appears likely that cationic polar cycloaddition proceeds via charge-transfer complexes.

Cationic polar cycloaddition[1,2] is characterized by being nearly always 100% regioselective and, where easily polarized unsymmetrical alkenes are involved, strongly stereoselective. Both of these selectivity effects appear to arise from the uneven distribution of the positive charge in the cation. One of the cycloaddition termini furnished by the cation is always the most positively polarized carbon in the molecule, while the other is more electron-rich and has no positive charge in any of the canonical forms contributing to the resonance hybrid.

A useful model for predicting the regiochemistry of polar cycloaddition requires the initial attack by the more negatively polarizable end of the alkene upon the most positive carbon atom of the cation. There is no difficulty in using this model to rationalize the regiochemistry of 19 of the 20 unsymmetrical addends which had been allowed to react with the acridizinium ion (**2**) at the time that the subject was last reviewed.[2]



1
2, R = H
3
4
5, R = H

That the 20th addend, acrylonitrile, adds with the β-carbon atom attacking the most positive carbon (position 6) of the acridizinium ion[3] was at first interpreted as indicating that polar influences are unimportant;[3] it was later rationalized by the suggestion[4] that *polarizability* and not ground-state polarization must be the determining factor in the regiochemistry of adduction. This opinion gains support from the frontier orbital calculations[5] which show that when acrylonitrile acts as a donor in cycloaddition the largest highest occupied molecular orbital (HOMO) coefficient is indeed that of the β-carbon atom of the double bond.

Since vinyl ethers have been shown to add to 2,3-dimethylisoquinolinium salts[6,7] and to the acridizinium ion[6] in a manner that is completely both regioselective and stereoselective (cf. **5**), it was felt important to learn more about the kinetics of this type of polar cycloaddition. With acridizinium derivatives significant correlations of the log of the relative rate of addition with the Hammett substituent constant, σ_p, were shown earlier for the addition of 9-substituted acridizinium perchlorate (**1**) to styrene[9] at 65 °C and to acrylonitrile[4] at 130 °C. In Table I are recorded the results of a similar study carried out at 0 °C using ethyl vinyl ether (**3**, R′ = Et) as the substrate. From the table it can be seen that the rate of reaction increases (over 100-fold) with the increase in the electron-withdrawing power of the 9 substituent on the acridizinium nucleus.

A Hammett plot (Figure 1) of the rate data was made using primary para substituent constants, where available, as well as the recommended statistical treatment.[12] Once again, a significant correlation (r = 0.995) was obtained. The electrophilicity of the acridizinium ion is clearly important whether the olefinic addend be a strong or weak nucleophile. A satisfactory correlation could not be obtained when Hammett σ_m constants were used.

In Table II can be seen a comparison of the reaction constants (ρ) obtained in studies of the rate of cycloaddition of various addends with 9-substituted acridizium derivatives; in each case ρ is based on primary σ constants, where available. As would be expected from its greater potential as an electron donor, ethyl vinyl ether gives a higher value of ρ than did the addends studied previously with the acridizinium ion, but the range of ρ values observed for the three vinyl addends is small considering the great change in polarity of the vinyl substituents. Significantly the value of ρ for ethyl vinyl ether is much smaller than the value of ρ (7.1) which has been reported[13] for the addition of vinyl ethers to tetracyanoethylene, a reaction believed to involve two steps.

Another method for studying polar influences on the cycloaddition of vinyl ethers is to use 4-substituted phenoxyethylenes (**3**, R′ = aryl). In Table III will be seen the results obtained when cycloaddition of phenoxyethylene with acridizinium perchlorate (**2**) was carried out at 65 °C in dimethyl sulfoxide.

Since the vinyl group is separated from the substituted phenyl ring by an oxygen atom, it would be predicted that the effect of the substituent would be inductive in nature. A satisfactory correlation of the reaction rates (r = 0.985) was made by a plot of log k/k_0 vs. the van Bekkum, Verkade, and Wepster[11] σ_n (Figure 2). The NMR spectra of the adducts examined did not permit us to determine whether the cycloaddition occurs stereoselectively as it has been shown[7] to do with alkyl vinyl ethers.

From activation parameters of some examples of the clas-

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Table I. Rates of Addition of Ethyl Vinyl Ether[a] to 9-Substituted Acridizinium Perchlorates (1) at 0 °C

9-Substituent, R	Registry no.	$k \times 10^3$, min^{-1}	σ_p[b]	Trials
Me	27705-56-2	0.71 ± 0.02	−0.170 ± 0.02[b]	3
H	18507-95-4	1.95 ± 0.07	0.000	3
F	1695-36-9	3.0 ± 0.2	0.062 ± 0.02[b]	3
Cl	1695-37-0	6.0 ± 0.1	0.227 ± 0.02[c]	3
COOMe	27705-64-2	12.8 ± 0.4	0.463 ± 0.02[d]	2
NO_2	27755-38-0	79.7 ± 3.9	0.778 ± 0.02[c]	2

[a] Registry no.: ethyl vinyl ether, 109-92-2. [b] Hammett para substituent constant. [c] Reference 10. [d] Reference 11.

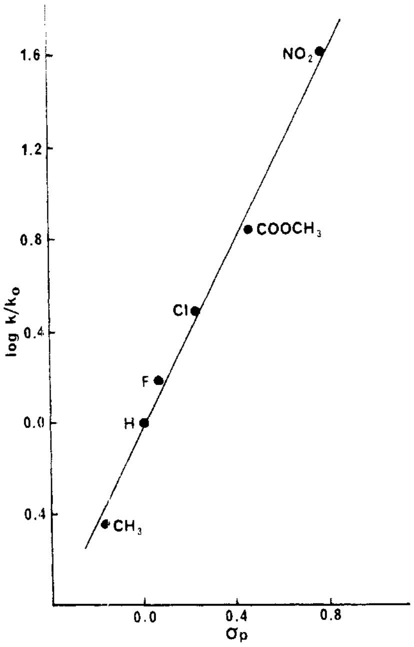
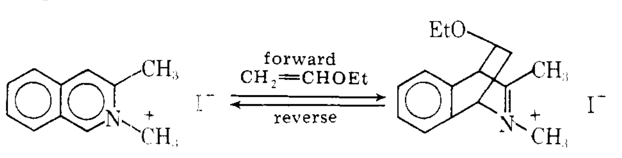


Figure 1. Plot of log k/k_0 for the cycloaddition of 9-substituted acridizinium perchlorates with ethyl vinyl ether vs. σ_p.

sical Diels–Alder reaction, it has been shown[14,15] that the geometry of the transition state for that reaction must be very similar to that of the adduct, and the generally accepted belief that the transition state is cyclic rather than linear is supported in at least one instance[15,16] by calculation of the entropies of activation for both possibilities.

Since the addition of ethyl vinyl ether to the 2,3-dimethylisoquinolinium ion (6) is easily reversible, the system



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promises to be useful for comparison of the activation parameters for the reverse and forward reaction for polar cycloaddition.

The forward reaction was carried out at 0 and 25 °C using pseudo-first-order conditions. The enthalpy of activation, $\Delta H^{\ddagger}_f$, for the forward reaction was found to be 14.6 kcal/mol, slightly higher than that for the average Diels–Alder reaction,[15] while the entropy of activation, $\Delta S^{\ddagger}_f = -32.2$ eu,[17] lies within the range reported for the classical Diels–Alder (forward) reaction[15] and suggests a highly ordered transition state.

The reverse reaction can be monitored at 62.5 and 104 °C, and the kinetics observed are first order. The enthalpy of activity of the reverse reaction, $\Delta H^{\ddagger}_r$ was 26.2 kcal/mol, or 11.6 kcal/mol higher than $\Delta H^{\ddagger}_f$, but still within the range of reported Diels–Alder reverse enthalpies.[15] The negative entropy of activation, $\Delta S^{\ddagger}_r = -2.4$ eu, was quite similar to that expected for a classical retro-Diels–Alder reaction.[15] Thus, the total picture shows a highly ordered transition state which must be very close in structure to the adduct. This similarity in reaction parameters to the classical Diels–Alder reaction suggests that in polar cycloaddition there is also a cyclic rather than a linear transition state, although the possibility of a two-stage reaction is not ruled out.

Table II. Hammett Reaction Constants (ρ) Obtained by Cycloaddition of Alkenes with 9-Substituted Acridizinium Ions

Alkene	Temp, °C	ρ	r	Ref
Acrylonitrile	130	1.13 ± 0.21	0.95	4
Styrene	65	1.69 ± 0.07	0.994	9
Ethyl vinyl ether	0	2.06 ± 0.11	0.995	

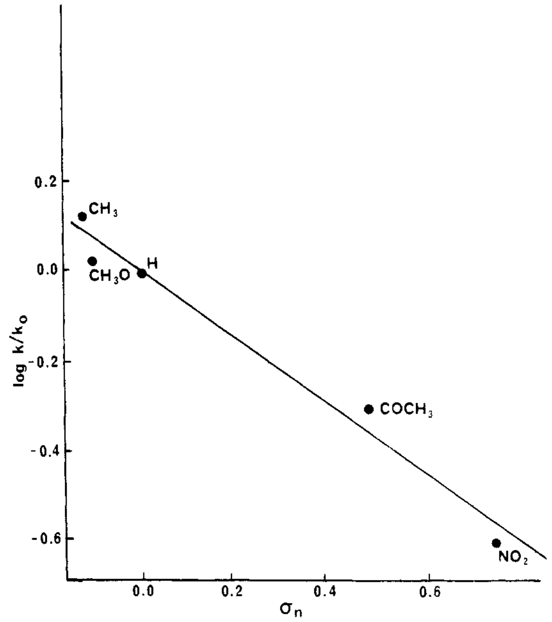


Figure 2. Hammett plot for the cycloaddition of acridizinium ion with aryl vinyl ethers at 65 °C using the σ_n of van Bekkum et al.

Table III. Rate Data for the Cycloaddition of Acridizinium Perchlorate by Phenoxyethylenes at 65 °C

Para substituent	Registry no.	σ_n[a]	$k \times 10^3$, min^{-1}
CH_3	1005-62-5	−0.14	8.47
OCH_3	4024-19-5	−0.11	6.67
H	766-94-9	0.0	6.41
$COCH_3$	1849-92-9	0.5	3.19
NO_2	940-14-7	0.77	1.55

[a] Reference 11.

The Mechanism of Cationic Polar Cycloaddition

A mechanism for cationic polar cycloaddition must account for each of the following observations. (1) Cationic polar cycloadditions are usually 100% regioselective,[2] and where readily polarizible electron-rich alkenes are involved, very stereoselective.[6-8] The regiochemistry observed is consistent with the attack of a cation on the more negatively polarized carbon of the olefinic bond, while the 100% stereoselectivity observed with the very polar alkenes is that which would be expected if there were an electrostatic repulsion between the quaternary nitrogen atom of the alkenophile and the center of positive charge in the polarized alkene. (2) In the acridizinium ion, position 6 plays a unique role in the rate-determining process. In the cycloaddition of styrene with the acridizinium cation having a methyl group at position 6, the negative entropy of activation is much larger than for one having a methyl group at position 11, the other terminus for cycloaddition.[18] There is a significant correlation (Table III) between the log of the relative rate (k/k_0) of cycloaddition and the Hammett para substituent constant (σ_p) (but not for σ_m) for the 9-substituted acridizinium system (**1**).[4,9] For 9-substituted acridizinium cations there is also a significant correlation between the relative rate of cycloaddition and the NMR chemical shift of the proton at position 6.[19] (3) In the cycloaddition of the acridizinium ion with para-substituted styrenes it is evident that the β carbon of the vinyl group plays a unique role in the rate-controlling process. The ^{13}C NMR chemical shifts of the β carbon of the vinyl group of the para-substituted styrenes give a significant correlation with the logarithm of that relative rate of cycloaddition, while the chemical shifts of the α carbon of the vinyl group do not (see Experimental Section). (4) Activation parameters for polar cycloaddition of 2,3-dimethylisoquinolinium ion and for the retro reaction are consistent with the parameters observed for cycloadditon and retro reaction in the classical Diels–Alder reaction. (5) There is no evidence that a carbonium ion exists as an intermediate in cationic polar cycloaddition. It is now clear that earlier claims from this laboratory[20] that the very slow addition of diethyl maleate to the acridizinium ion in the presence of sodium acetate to give a mixture of cis and trans addition products are erroneous and a consequence of undetected fumarate in the (excess) maleate used. While the study of the geometrical isomer of a more reactive 1,2-disubstituted ethylene should be carried out, it seems unlikely that any lack of stereospecificity will be observed. Neither external nor internal carbonium ion traps have provided evidence for the existence of carbonium ion intermediates in cationic polar cycloaddition. With the acridizinium ion, norbornadiene gives a 90% yield of simple 1,4-addition products[21] without any evidence of the presence of nortricyclene derivatives. As pointed out earlier, this must either indicate the lack of a carbonium ion intermediate or (as now seems much less likely) one which exists for an extremely short lifetime. Since some type of sterochemical sorting-out process must be involved in a cycloaddition which (in some cases) is 100% stereoselective, a carbonium ion, in particular one that is unusually short-lived, would seem an inadequate intermediate.

In summary, the mechanism for cationic polar cycloaddition must rationalize the obvious regiochemical and stereochemical resemblance to the attack of a cation on a polarized alkene with the absence of any evidence for an intermediate carbonium ion and with the existence of reaction parameters which suggest a concerted cycloaddition reaction. The most plausible explanation, and one put forward earlier[22] in a more tentative manner, is that charge-transfer complexes exist as intermediates or as stages along the reaction pathway in cationic polar cycloaddition.

Aromatic quaternary salts are known[23,24] to play an acceptor role in charge-transfer complex formation with electron-rich donors. For example, the 2-methylisoquinolinium ion has been reported to form such complexes with iodide ion,[25] dimethylaniline,[26] polycyclic hydrocarbons,[27] or isoquinoline.[28] Indeed the phenomenon is so general that it would be difficult to doubt that π complexes exist between alkenes and the cations (e.g., **2** and **6**) which undergo polar cycloaddition with them. The question on which there is no consensus is whether the observed complexes are relevant to the mechanism of polar cycloaddition.

Considering the mechanism of the classical Diels–Alder reaction, Woodward[29] quite early arrived at the conclusion that the initial interaction leading to cycloaddition involved charge-transfer complexes. The explanation was accepted by Kloetzl[30] in a review of the cycloaddition reactions of maleic anhydride. More recent reviewers of both the Diels–Alder reaction[31] and of charge-transfer complexes[32] give serious consideration to the possible role of such complexes in cycloaddition. Konovalov[33] et al. have shown that there is a linear relationship between the rates of reaction of a series of *N*-arylmaleimides and their abilities to form charge-transfer complexes with *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine, and Tyutyulkov and Markov,[34] from LCAO–MO calculations, have shown that a π complex is formed between maleic anhydride and various condensed aromatic hydrocarbons and that a correlation exists between the delocalization energy of the π complex and the corresponding values for Brown's para-delocalization energy, which is in turn a useful measure of Diels–Alder reactivity.[35]

One of the most important recent theoretical developments in connection with cycloaddition has been the application of the frontier orbital approach.[36-39] This method has been used successfully to account for reaction rates and regioselectivity by considering the interaction of the highest occupied molecular orbital (HOMO) of the donor and the lowest unoccupied molecular orbital (LUMO) of the acceptor. It is pertinent that consideration of the same type of HOMO–LUMO interaction has been used successfully in explaining the formation of charge-transfer complexes.[40] In a recent rationalization of cycloaddition behavior by use of Hückel frontier orbitals, Mok and Nye[41] have taken as a premise that charge-transfer complexation occurs along the reaction coordinate for cycloaddition.

In cationic polar cycloaddition the observations made to date can be explained in terms of isomeric transition states which are either charge-transfer complexes or closely related to such ion structure. The differences in the energies of activation for reaction via the several regioisomeric and stereoisomeric transition states must, in most cases, arise from differences in the polar influences lying along the reaction pathway. These polar influences include the initial frontier orbital interaction.

Like the isoquinolinium ion (**6**), the acridizinium ion (**2**) appears to form weak charge-transfer complexes. When 1,2-dimethoxybenzene (veratrole) was added to acridizinium perchlorate in dimethyl sulfoxide solution there was a marked intensification of the usual yellow color and the visible absorption spectrum of the mixture was not that which results from the addition of the spectra of pure samples of the two solutes. There was a slight (4%) decrease in the absorption at 399 nm, but a more dramatic change occurred in the longer wavelength range. Whereas the uncomplexed acridizinium ion gave no perceptible absorption beyond 435 nm, at the same concentration the acridizinium ion to which 1,2-dimethoxybenzene had been added continued to absorb to about 470 nm. It was noted also that the addition of dimethoxybenzene completely quenched the fluorescence of the acridizinium ion, as does the addition of electron-rich olefins.

Like the Diels–Alder reaction in which only certain of the

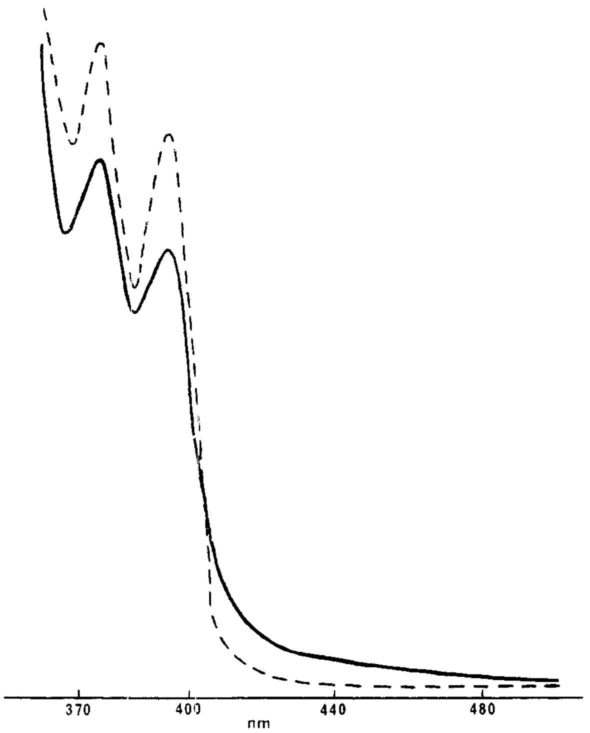
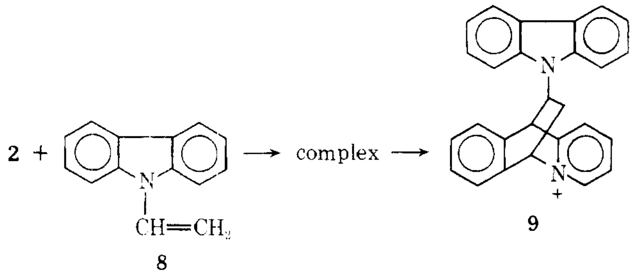


Figure 3. (A) The sum of the absorptions of individual acetonitrile solutions, one 5×10^{-4} M in acridizinium tetrafluoroborate and the other 0.2 M in *N*-vinylcarbazole (- -). (B) Absorption of a combined solution of 5×10^{-4} M in acridizinium tetrafluoroborate and 0.2 M in *N*-vinylcarbazole (–).

donor–acceptor combinations give perceptible transient color changes, only two of the more reactive alkenes studied produced similar transient color changes with the acridizinium ion. The two alkenes which showed color with the acridizinium ion were 1-morpholino-1-phenylethylene and *N*-vinylcarbazole (**8**). The latter alkene (**8**) underwent cycloaddition to form **9** slowly enough to permit a convenient quantitative spectroscopic study of complex formation. Figure 3 shows the sum of the individual absorptions for a 5×10^{-4} M acetonitrile solution of acridizinium tetrafluoroborate and of a 0.2 M solution of *N*-vinylcarbazole as curve A. Curve B is for a mixture in which the two components are present at the same concentrations. Whereas the sum of the individual spectra (curve A) showed no perceptible absorption beyond 435 nm, the vinylcarbazole–acridizinium mixture (curve B) continued to absorb beyond 480 nm, a characteristic evidence[42] of charge-transfer interaction. This tailing of the spectrum arises from a lowering of the energy[43] of the π^* orbital (lowest unoccupied molecular orbital) in the acridizinium ion. Since this is the orbital of the acridizinium ion most closely involved in cycloaddition reactions,[44] the change is in accord with predictions based on frontier orbital theory.[36b,38b,45] Frontier orbital theory may also explain[46] the quenching of fluorescence observed when acridizinium ion is treated with vinylcarbazole or other electron-rich molecules.



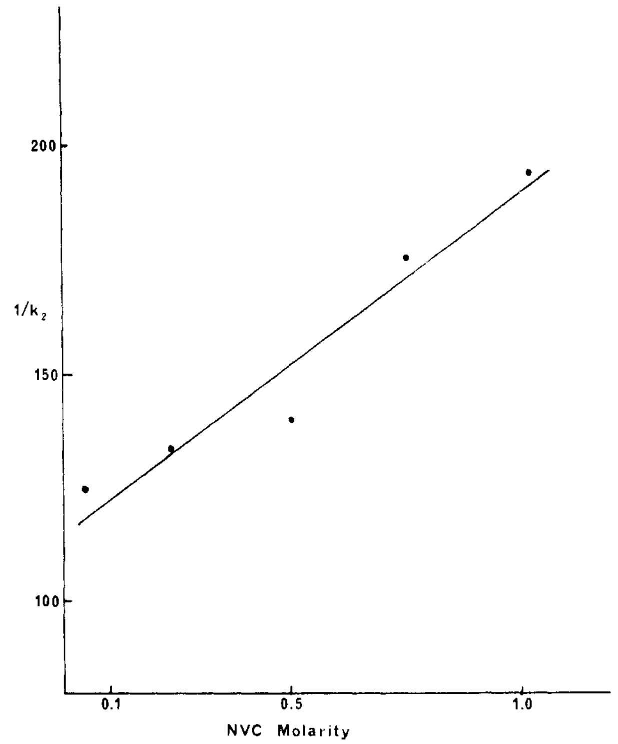


Figure 4. Second-order rate constants, *k* (mol^{-1} L s^{-1}), for the reaction of NVC (*N*-vinylcarbazole) with a 0.005 M solution of acridizinium tetrafluoroborate.

As a possible test for complex formation during cycloaddition, Andrews and Keefer[47] determined whether the pseudo-first-order rate constants obtained when an excess of maleic anhydride (or chloromaleic anhydride) reacted with 9,10-dimethylanthracene increased directly with an increasing concentration of the anhydride and whether the apparent second-order rate constant remained constant under these conditions. The failure of the reaction to meet these tests was offered as evidence that a considerable quantity of the hydrocarbon was complexed.

A parallel behavior has been observed for the cycloaddition of the acridizinium ion in the presence of excess *N*-vinylcarbazole in the concentration range found to give pseudo-first-order kinetics. A plot (Figure 4) of the apparent second-order rate constant vs. olefin concentration shows the expected decline in the rate constant with increased concentration of the olefin ($r = 0.97$). Following the treatment of Andrews and Keefer,[47] an equilibrium constant, $K = 0.65$ mol^{-1} L, was obtained for the complexation reaction.

A possible alternative explanation for the observed change in rate constant might be that polar cycloadditions may be highly susceptible to slight changes in the polarity of the solvent, such as those produced when the concentration of the alkene is changed. While the effect of solvent polarity on the rate of cycloaddition of the acridizinium ion with *N*-vinylcarbazole has not been studied, it is known that for the addition of styrene to the same substrate the ratio of the rate of addition in ethyl acetate to that in dimethyl sulfoxide is only 1.3, indicating that great changes in solvent polarity have but little effect on the rate of polar cycloaddition. There is certainly no evidence for the existence of the extremely large effects of solvent polarity which would be needed as an alternate explanation for the apparent change in the second-order rate constant shown in Figure 4.

While the demonstration that a charge-transfer complex exists when a very reactive alkene adds to the acridizinium ion, it does not prove that the complex is an intermediate rather than an irrelevant side reaction[48] of the cycloaddition. In view

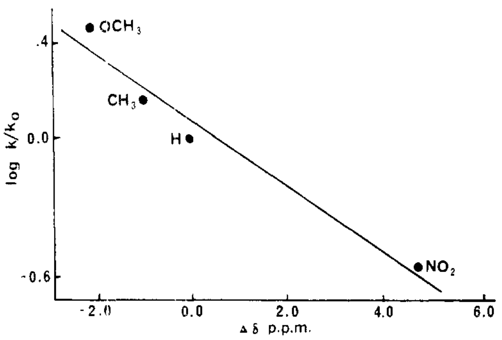
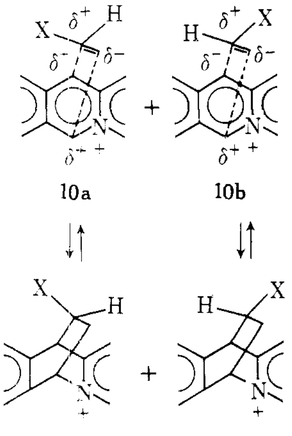


Figure 5. Plot of log k/k_0 vs. the reported[55] ^{13}C NMR chemical shift values for the β carbon of para-substituted styrenes.

of the successful application of frontier orbital calculations to both charge-transfer complex formation[49] and to cycloaddition,[34-37] it would seem remarkable if for a single cation there were two distinct types of frontier electron interaction, one leading only to complex formation and the other exclusively to cycloaddition. Since a charge-transfer complex can form without the creation of a true σ bond, no carbonium ion need be formed. The orientation of this molecular complex (**10a** or **10b**) must determine both the regiochemistry and stereochemistry of the adducts (**11a** or **11b**). If X represents a group which can easily release electrons, the center of positive charge of the alkene moiety of the complex (**10**) would lie further along the C–X bond than if the group were less polarizable. In a complex in which such a polarization of the C–X band had occurred, coulombic repulsion would make geometrical isomer **10a** of lower energy than **10b**, in which the centers of positive charge lie closer together. The differences in energy between **10a** and **10b** would not be large even for highly polarized X groups, and it is not remarkable that when X is less highly polarizable, addition occurs with only moderate stereoselectivity.



10a 10b

11a 11b

Arguments offered for the existence of charge-transfer complexes in the the classical Diels–Alder reaction[41] where both donor and acceptor molecules are uncharged become even more cogent in the case of cationic polar cycloaddition in which the acceptor is actually a cation. Certainly the proposal of a π complex preceding σ-bond formation is consistent with currently accepted[50] mechanisms for the addition of other cationic reagents to alkenes and affords the best explanation of how a cation can participate in essentially a two-stage reaction without the creation of an intermediate carbonium ion.

Experimental Section

Melting points were taken in capillary tubes with a Thomas-Hoover melting point apparatus and are uncorrected. Proton magnetic resonance spectra were determined with a Varian A-60 or T-60 instrument or a Joelco MH 100 spectrometer using tetramethylsilane as an internal standard. A Beckman Model DB-G spectrometer was used to measure the rates of addition or cycloreversion.

Rates of Cycloaddition of Ethyl Vinyl Ether to 9-Substituted Acridizinium Perchlorates (1). The 9-substituted acridizinium derivatives were prepared as previously described.[9] All solvents were freshly distilled before use. A small quantity of hydroquinone was added to the stock solutions of ethyl vinyl ether to retard polymerization.

To 1 mL (0.05 mmol) of a 0.05 M solution of the substituted acridizinium perchlorate in acetonitrile at 0 °C was added 1 mL (0.5 mmol) of 0.5 M ethyl vinyl ether in acetonitrile at 0 °C. The mixture was maintained at 0 ± 0.2 °C by use of an ice bath (Dewar flask). The progress of the reaction was followed by observing the disappearance of the absorption (A) at the long wavelength maximum in the visible spectrum. Samples were prepared by a 100 μL/50 mL dilution with 95% ethanol. The rate for each trial was obtained by a nonweighted least-squares fit of $-\log A$ vs. time. The reported rate (Table I) is an average of 2–3 trials.

Phenoxyethylenes (3). All of the phenoxyethylenes used in our study are known compounds prepared by the action of potassium *tert*-butoxide on the appropriate 2-bromoethyl phenyl ether essentially following the directions given by Dombroski[51] for the preparation of 4-nitrophenoxyethylene.

The method of purification and observed physical constants of the vinyl ethers follow.

Phenyl: by repeated distillation, bp 30 °C (0.4 mm) [lit.[52] bp 54 °C (17 mm)]; IR (neat) 6.04, 6.24, 6.68, 7.18, 7.60, 8.04 (brd), 8.60 (brd), 9.24 (s), 10.40 (brd), 11.64, 12.44, 13.24, 14.44 μm.

***p*-Nitrophenyl:** by chromatography on silica gel using 30–60 °C petroleum ether followed by benzene as eluents and sublimation followed by recrystallization, nearly colorless, mp 56–58 °C (lit.[51] 55–56 °C); NMR ($CDCl_3$) δ 4.8 (complex, 2, vinyl), 6.61 (q, 1, vinyl), 7–9.1 (complex, 4, aromatic).

***p*-Tolyl:** by distillation, bp 44–46 °C (0.6 mm) [lit.[52] 72.5 °C (17 mm)], followed by chromatography on silica gel; NMR ($CDCl_3$) δ 2.27 (s, 3, Me), 4.5 (complex, 2, vinyl), 6.6 (q, 1, vinyl), 7.0 (q, 4, aromatic).

***p*-Methoxyphenyl:** by distillation, bp 53–54 °C (0.8 mm) [lit.[52] 91.0–91.5 °C (12 mm)], and further purified by column chromatography on silica gel; NMR ($CDCl_3$) δ 3.76 (s, 3, Me), 4.50 (complex q, 2, vinyl), 6.61 (q, 1, vinyl), 6.95 (d, 4, aromatic).

***p*-Acetylphenyl:** by distillation, bp 81–85 °C (0.4 mm) [lit.[53] bp 128.5 °C (13 mm)], and chromatography on silica gel; NMR ($CDCl_3$) δ 2.52 (s, 3, Me), 4.78 (complex q, 2, vinyl), 6.75 (q, 1, vinyl), 7.1–8.02 (complex, 4, aromatic).

Rates of Cycloaddition of Phenoxyethylenes to the Acridizinium Ion (2 → 5) at 65 °C. The rate studies were carried out in dimethyl sulfoxide solution as described earlier for the cycloaddition of styrene,[9] a ratio of 10 mol of phenoxyethylene to 1 mol of acridizinium being used to assure pseudo-first-order kinetics. Each rate was measured in triplicate and was reproducible within approximately 5%. With p-nitrophenoxyethylene a small correction factor was needed to compensate for absorption by the olefin at 397 nm. Correlation coefficients for plots of ln $1/A$ vs. time were in all cases greater than 0.99. The data are recorded in Table III.

Adducts (5, R′ = Aryl) Obtained by Reaction of Acridizinium Perchlorate (2) with Aryl Vinyl Ethers. (A) With *p*-Methoxyphenyl (3, R′ = *p*-$CH_3OC_6H_4$): A mixture containing 0.5 g of acridizinium perchlorate[54] and 0.3 g of p-methoxyphenyl vinyl ether in 50 mL of acetonitrile was refluxed for 18 h. The solvent was removed under vacuum, and the residue was triturated with ether. A portion of the resulting solid was reserved for NMR analysis and a portion recrystallized from ethanol, mp 218–219 °C; NMR (crude product in $CDCl_3$) δ 1.78 (s, 3), 5.05 (brd s, 1), 5.57 (d, 1), 6.6–8.6 (complex, 14), 9.30 (d, 1).

Anal. Calcd for $C_{22}H_{20}NClO_6$: C, 61.47; H, 4.69; N, 3.26. Found: C, 61.43; H, 4.72; N, 3.03.

(B) With *p*-Nitrophenyl (3, R′ = *p*-$NO_2C_6H_4$): The acridizinium adduct (5, R′ = p-$NO_2C_6H_4$) was prepared similarly, mp 218.5–220 °C.

Anal. Calcd for $C_{21}H_{17}N_2ClO_7$: C, 56.70; H, 3.85; N, 6.30. Found: C, 56.51; H, 3.71; N, 6.22.

Activation Parameters for the Cycloaddition of 2,3-Dimethylisoquinolinium Iodide (6) with Ethyl Vinyl Ether. The rate constants for the cycloaddition were determined at 0 °C as described earlier[19] and in essentially the same way at 25 °C. The enthalpy of activation was calculated from plots of ln k/T vs. $1/T$. The $\Delta G^{\ddagger}{}_{f}$ and $\Delta S^{\ddagger}{}_{f}$ were calculated by means of eq 1 and 2. The observed rate constants were 0.062 ± 0.002 × 10^3 min^{-1} at 0 °C and 0.61 ± 0.006 × 10^3 min^{-1} at 25 °C.

$$k = \frac{KT}{h} e^{-\Delta G^{\ddagger}/RT} \qquad (1)$$

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger} \qquad (2)$$

Activation Parameters for the Cycloreversion of the 2,3-Dimethylisoquinolinium Iodide–Ethyl Vinyl Ether Adduct (7). In a three-neck round-bottom flask equipped with a nitrogen inlet tube, stopper, condenser, and a magnetic stirring bar was placed 50 mL of dimethylformamide, and the gas inlet tube was adjusted so that nitrogen bubbled slowly through the liquid. The flask was heated in a silicone oil bath at 62.5 ± 0.5 °C (or 104 ± 0.5 °C). When the flask and its contents had reached bath temperature, 89.0 mg (0.250 mmol) of the cycloadduct was added, and the mixture was stirred vigorously with nitrogen bubbling slowly through the solution. The progress of the decomposition was followed by observing the increase of the long wavelength absorption in the UV spectrum of the 2,3-dimethylisoquinolinium ion. Samples slightly larger than 100 μL were withdrawn and cooled in ice. Exactly 100 μL of the cold solution was diluted to 10 mL with 95% ethanol for the UV analysis. The rates were obtained by plotting −log (cycloadduct) vs. time. The rate constants ($k \times 10^3$ min^{-1}) were found to be 1.08 at 62.5 °C and 93.8 at 104 °C.

Correlation of Log of Relative Rate (k/k_0) for Cycloaddition of Para-Substituted Styrenes with Published Data for the ^{13}C Chemical Shifts. The availability[55] of C_α and C_β ^{13}C chemical shifts for several para-substituted styrenes made it possible to determine whether these parameters were related to the relative rate of cycloaddition[56] of these styrenes with acridizinium perchlorate. The rate constants (×10^{-2} min^{-1}) observed at 100 °C for the reaction of the para-substituted styrenes with acridizinium perchlorate were as follows: MeO, 15.0 ± 0.7; Me, 7.4 ± 0.4; H, 5.1 ± 0.3; NO_2, 1.5 ± 0.1. A plot of log k/k_0 vs. the reported ^{13}C chemical shifts of the β carbon of the styrene side chain is shown in Figure 5. The correlation constant ($r = 0.985$) shows an acceptable[12] correlation ($r \geqq 0.95$). The slope of the line is 0.14 ± 0.02 Hz^{-1}. A similar plot of log k/k_0 vs. the ^{13}C chemical shift of the α carbon of the styrene side chain has a slope of 0.35 ± 0.38 Hz^{-1} and an unacceptable correlation constant of 0.61.

Investigation of Charge-Transfer Interaction. The acetonitrile used as solvent was shown to be transparent in the spectral range studied. Separate stock solutions of acridizinium tetrafluoroborate, 1 × 10^{-3} M, and thrice recrystallized N-vinylcarbazole, 0.4 M, were prepared. Individual spectra were made after dilution of the proper stock solution with an equal volume of solvent, while the solution of the complex was made by addition of equal volumes of the two stock solutions. The spectra are shown in Figure 3.

The rate studies were again carried out essentially as described earlier[9] using a constant acridizinium tetrafluoroborate concentration of 0.005 M in dimethyl sulfoxide solution and various concentrations of thrice recrystallized N-vinylcarbazole. The reaction was monitored by dilution of 100-μL aliquots to 5 mL with methanol and measuring the absorption at 395 nm using 1-cm quartz cells. Pseudo-first-order kinetics were observed at all of the N-vinylcarbazole concentrations studied. A plot of the change in second-order rate constant with change in N-vinylcarbazole concentration is shown in Figure 4. The treatment of Andrews and Keefer[47] was followed in the calculation of the equilibrium constant.

Effect of Solvent Polarity on the Rate of Cycloaddition of Styrene with Acridizinium Hexafluorophosphate. Stock solutions, each 1.0 × 10^{-4} M in the acridizinium salt, were prepared using ethyl acetate or dimethyl sulfoxide as the solvent. To 150 mL (1.5 × 10^{-5} mol) of the acridizinium salt solution was added 4.3 mL (3.75 × 10^{-2} mol) of styrene, and the mixture was heated in a thermostat at 66 °C. Samples were withdrawn periodically, cooled rapidly, and transferred directly to a spectrophotometer cell. Calculations made in the usual way gave pseudo-first-order rate constants k(ethyl acetate) = 9.1 × 10^{-3} min^{-1} and k(dimethyl sulfoxide) = 6.8 × 10^{-3} min^{-1}.

Registry No.—N-Vinylcarbazole, 1484-13-5; **5** (R′ = p-$MeOC_6H_4$), 64740-21-2; **5** (R′ = p-$NO_2C_6H_4$), 64682-17-3; **6**, 32431-36-0; **7**, 64682-18-4; p-methoxystyrene, 637-69-4; p-methylstyrene, 622-97-9; styrene, 100-42-5; p-nitrostyrene, 100-13-0.

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