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Kinetics and Mechanism of Aminium Salt Initiated Cycloadditions

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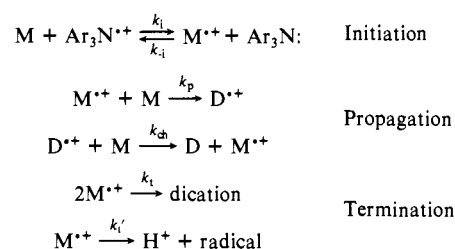
Abstract: The kinetics of aminium salt initiated cycloadditions has been studied and the previously proposed cation-radical chain mechanism verified. Temperature-dependence studies have provided the first experimental measurements of activation parameters for cation radical/neutral cycloadditions. Consistent with theoretical calculations, these reactions have extraordinarily low (<5 kcal/mol) activation energies. The rate retardation engendered by added tris(4-bromophenyl)amine is observed to be specific for cation-radical chain mechanisms, as opposed to, e.g., Brønsted acid-catalyzed mechanisms and is proposed as a general kinetic criterion for the cation-radical chain mechanism.

Potent catalysis/initiation of a variety of Diels–Alder and cyclobutanation reactions by triarylaminium salts has been observed in this laboratory[1-4] and interpreted in terms of a cation-radical chain mechanism.[1,5] The observation that most of these same cycloadditions can be accomplished under photosensitized electron-transfer (PET) conditions well-known to generate cation radicals lends strong support to this mechanistic proposal.[6,7] The aminium salt and PET-induced reactions exhibit remarkable correspondence in terms of Diels–Alder vs. cyclobutane selectivity, endo–exo selectivity, regiospecificity, and chemoselectivity. In only one instance have the two reactions been found to diverge with respect to a selectivity element, and this is now known to involve an aminium salt induced, Brønsted acid-catalyzed cycloaddition.[8] Theoretical considerations, including the calculation of vanishingly low activation energies for prototype cation-radical cycloadditions to neutral molecules are also consistent with the proposed mechanism.[9-11] The kinetic/mechanistic studies reported herein provide compelling kinetic evidence for the cation-radical chain mechanism of aminium salt initiated cycloadditions and permit mechanisms involving either Brønsted acid catalysis or an aminium salt–π-substrate complex (as opposed to complete electron transfer producing a π-substrate cation radical) to be ruled out. Further details of the chain mechanism, including the nature of the termination steps, are also clarified. Activation parameters for the overall reaction have been determined and those for the cycloaddition step approximated using electrochemical potentials, thus affording the first experimental measurements of activation parameters for a cation-radical/neutral cycloaddition.[12]

Results and Discussion

The kinetics of the Diels–Alder cyclodimerization of 1,3-cyclohexadiene (1) in dichloromethane (3.5×10^{-3} to 7.0×10^{-4}

Scheme I[a]

$$M + Ar_3N^{\bullet+} \underset{k_{-i}}{\overset{k_i}{\rightleftarrows}} M^{\bullet+} + Ar_3N: \quad \text{Initiation}$$

$$M^{\bullet+} + M \xrightarrow{k_p} D^{\bullet+}$$

$$D^{\bullet+} + M \xrightarrow{k_{ch}} D + M^{\bullet+} \quad \text{Propagation}$$

$$2M^{\bullet+} \xrightarrow{k_t} \text{dication}$$

$$M^{\bullet+} \xrightarrow{k_t'} H^+ + \text{radical} \quad \text{Termination}$$

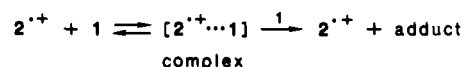[a] Where **M** = **1** or **3**; D = cyclodimer.

Scheme II. Proposed Termination Steps in the Cyclodimerizations of **1** and **3**

Scheme III

$$2^{\bullet+} + 1 \rightleftharpoons [2^{\bullet+}\cdots 1] \xrightarrow{1} 2^{\bullet+} + \text{adduct}$$
$$\text{complex}$$
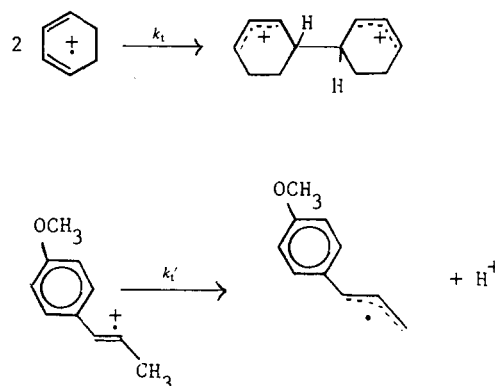
M) initiated by tris(4-bromophenyl)aminium hexachloroantimonate ($2^{\bullet+}$, 10–20 mol % relative to **1**)[13] was studied in the temperature range 0–25 °C using a Hewlett-Packard 8450A diode array UV/visible spectrophotometer. The yield of Diels–Alder dimers under these conditions was nearly quantitative (95%). The experimental rate law (rate = $k_{app}[1]^{3/2}[2^{\bullet+}]^{1/2}$) is invariant over the substantial range of diene and catalyst concentrations and temperatures cited above. Although a wide variety of other possible rate laws were explored, none adequately fitted the data except that given above. This rate law, typical of many radical-chain processes,[14] is precisely that derived for the proposed

(1) Bellville, D. J.; Wirth, D. W.; Bauld, N. L. *J. Am. Chem. Soc.* **1981**, *103*, 718.

(2) Bellville, D. J.; Bauld, N. L.; Pabon, R. A.; Gardner, S. A. *J. Am. Chem. Soc.* **1983**, *105*, 3584.

(3) Pabon, R. A.; Bellville, D. J.; Bauld, N. L. *J. Am. Chem. Soc.* **1984**, *106*, 2730.

(4) Bauld, N. L.; Pabon, R. A. *J. Am. Chem. Soc.* **1983**, *105*, 633.

(5) Bell, F. A.; Crellin, R. A.; Fuji, N., Ledwith, A. *Chem. Commun.* **1969**, 251.

(6) Jones, C. R.; Allman, B. J.; Mooring, A.; Spahic, B. *J. Am. Chem. Soc.* **1983**, *105*, 1982.

(7) Pabon, R. A.; Bellville, D. J.; Bauld, N. L. *J. Am. Chem. Soc.* **1983**, *105*, 3584.

(8) Gassman, P. G.; Singleton, D. A. *J. Am. Chem. Soc.* **1984**, *106*, 7993.

(9) Bauld, N. L.; Bellville, D. J.; Pabon, R. A.; Chelsky, R.; Green, G. *J. Am. Chem. Soc.* **1983**, *105*, 2378.

(10) Pabon, R. A.; Bauld, N. L. *J. Am. Chem. Soc.* **1984**, *106*, 1145.

(11) Bellville, D. J.; Bauld, N. L. *Tetrahedron*, submitted for publication. An ab initio theoretical study of the role-reversed cation-radical Diels–Alder.

(12) A bimolecular rate constant of 3×10^8 M^{-1} s^{-1} has been estimated for the cycloaddition of the cyclohexadiene cation radical to cyclohexadiene in photochemical quenching experiments: Calhoun, G. C.; Schuster, G. B. *J. Am. Chem. Soc.* **1984**, *106*, 6870.

(13) The aminium salt catalyst is available from the Aldrich Chemical Co.

(14) The rate law may be viewed as reflecting a first-order dependence on the monomer (**1**) and a one-half order dependence on the initiator system (**1** + **2**$^{\bullet+}$): Walling, C. *Free Radicals in Solution*; Wiley: New York, 1957; p 67, for example).

Table I

M	t (°C)	k_{app}	$\Delta H^{\ddagger}_{app}$ (kcal)	$\Delta S^{\ddagger}_{app}$ (eu)	$\Delta G^{\ddagger}_{app}$ (kcal)	$\Delta H^{\ddagger}_{p}$ (kcal)
1	25.0	12.87 ± 2.63	7.95 ± 0.46	−26.87 ± 1.57	15.57 ± 0.91	1.61 ± 0.09
	17.0	7.75 ± 0.84				
	10.0	6.10 ± 0.11				
	0.0	3.34 ± 0.15				
	25.0[a]	5.88				
		k_{app} (×10⁻⁴)				
3	25.0	5.04 ± 0.39	2.14 ± 0.13	−29.85 ± 1.78	10.59 ± 0.63	0.76 ± 0.04
	17.0	4.55 ± 0.23				
	10.0	3.91 ± 0.14				
	0.0	3.35 ± 0.16				
	25.0[b]	1.52				

[a] Rate in presence of 25 mol % of **2** (free triarylamine). [b] Rate in presence of 100 mol % of **2**.

cation-radical chain mechanism (Scheme I), assuming a bimolecular chain-termination step. The most likely termination step therefore is a bimolecular coupling of **1**[•+] to produce a dication (Scheme II). The derivation of the indicated rate law styles the rate as rate = $-d[1]/dt = 2k_p[1][1^{•+}]$ and utilizes the steady-state approximation to obtain both [**1**[•+]] and [D[•+]], where the latter is the concentration of the cation radical of the Diels–Alder dimer. The detailed derivation of this rate law is given in the Appendix. It will be evident that this simple rate law is valid only at relatively low [2]/[1] ratios, where back-transfer of an electron from neutral triarylamine **2** to **1**[•+] is much slower than the propagation step involving cycloaddition of **1**[•+] with **1**. This stipulation is adequately fulfilled, since at the beginning of the reaction no **2** is present, and, although the decomposition of **2**[•+] does gradually generate some **2**, multicomponent analysis confirms that the ratio of [2]:[1] never exceeds 0.1 over the reaction time monitored (ca. 0–40% reaction). Of course, addition of larger amounts of triarylamine at the start of the reaction does induce reversibility in the initiation step and engenders large rate reductions (Table I). This observation is inconsistent with an alternative mechanism which postulates complexation of the aminium salt with **1**, followed by reaction of the latter complex with **1** (Scheme III). Such a reaction should be unaffected by added triarylamine. Instead, complete electron transfer from **1** to **2**[•+], forming **1**[•+], is indicated. Furthermore, the kinetic rate law for the complex mechanism is second order in the diene and first order in the aminium salt, neither of which is found for the dimerization of 1,3-cyclohexadiene. A rate-determining formation of the complex is also excluded by the rate law. As will be discussed further on, rate diminution by added neutral triarylamine appears to be a useful, general diagnostic for cation-radical chain mechanisms.

Analogous observations have been made for the cyclodimerization of *trans*-anethole (**3**)[4] except that the rate law here (rate = $k_{app}[3]^2[2^{•+}]$) requires unimolecular termination by **3**[•+] in contrast to the result obtained in the dimerization of **1**. The implication of this observation appears to be that termination in this case occurs by deprotonation of **3**[•+] (Scheme II). Once more rate depression by added triarylamine appears to clearly rule out a complex-type mechanism.

Temperature-dependence studies of the cyclodimerization of both **1** and **3** reveal the expected large negative entropies of activation (Table I). As predicted theoretically, the activation enthalpies are extraordinarily low (7.95 and 2.14 kcal/mol, respectively). These latter, of course, are composite quantities. If exothermic electron-transfer steps and termination are assumed to be approximately diffusion controlled, the overall activation enthalpies can be analyzed into contributions from the cycloaddition step (ΔH_p) and from initiation (ΔH_i). The latter can be approximated using electrochemical oxidation potentials. The (reversible) oxidation potential of **2** in dichloromethane vs. SCE is found, in this work, to be 1.05 V. Reversible potentials for the oxidation of **1** and **3** could not be obtained, even using cyclic voltammetry, but the peak potentials, also measured in dichloromethane vs. SCE, are 1.60 and 1.11 V, respectively. Deducting the contribution of these (initiation) steps from the overall activation enthalpies affords estimates of the activation enthalpies (ΔH_p) for the cycloaddition steps. These are found to be 1.61

Table II. Effect of Additives on the Cyclodimerization Rate of **1** at 10 °C

additive[a]	rate (k_{app})	additive[a]	rate (k_{app})
none	6.10	octanal	4.67
acetonitrile	4.96	isopropyl alcohol	2.92
diethyl ether	4.83	triethylamine	0.

[a] Additives were present at 100 mol % relative to **1**.

and 0.76 kcal/mol, respectively, assuming equal ΔS_i for the oxidation of **1–3**.[15] For a crude comparison, the activation enthalpies of the prototype neutral Diels–Alder and cyclobutanation reactions are 34.3[16] and 62.5[17] kcal/mol, respectively. The corresponding catalytic factors are impressive (10^{23} and 10^{49}).

No kinetic data concerning the effect of various functional groups on cation-radical chain reactions have previously been reported. A priori, it might be expected that both nucleophiles and single electron donors would inhibit the reaction by interception of the chain-carrying cation radicals. The data in Table II confirm that isopropyl alcohol substantially, and triethylamine powerfully, inhibit the cycloaddition of **1** at additive concentrations equivalent to the concentration of **1**. Acetonitrile, diethyl ether, and octanal exert smaller effects which may be the result of solvation of the cation radicals by the polar functional groups present in these molecules, although mild inhibition remains a possibility.

Rate retardation by added **2** promises to be a useful diagnostic for cation-radical chain reactions. In contrast to the retardations observed in the cyclodimerizations of **1** and **3**, the rate of the aminium salt induced cyclodimerization of 2,4-dimethyl-1,3-pentadiene is unaffected by added **2**. This reaction had previously been determined to occur via a Brønsted acid-catalyzed mechanism.[8] The present results provide the necessary confirmation that **2** is not protonated by the strong acids generated during aminium salt induced cycloadditions and, as expected, does not interfere with such Brønsted acid-catalyzed reactions. The observed kinetic rate law for the dimerization of 2,4-dimethyl-1,3-pentadiene ($R = k[Ar_3N^{•+}][D]$) is indeed compatible with a Brønsted acid-catalyzed reaction in which the Brønsted acid is the cation radical of the diene or derives from this cation radical by a first-order process (deprotonation). The reaction is, of course, completely suppressed by the addition of 2,6-di-*tert*-butylpyridine in a molar amount equal to or exceeding that of the aminium salt.[8]

The chain lengths for the cyclodimerizations of both **1** and **3** are found to be approximately 20. While not long, these chain lengths do appear to be sufficient to warrant the kinetic treatment derived here.

Experimental Section

Solvents and Reagents. Dichloromethane (Aldrich, HPLC grade) was further dried and purified by distillation from P_2O_5 under dry N_2. It was

(15) A small contribution to $\Delta G^{\ddagger}_p$ in the amount of $RT \ln (\sqrt{2})$ is arbitrarily assigned to $\Delta S^{\ddagger}_i$ in the case of **1**. This amounts to only −0.19 kcal/mol.
(16) Townshend, R. E.; Ramunni, G.; Segal, G.; Hehre, W. J.; Salem. L. *J. Am. Chem. Soc.* **98, 1976,** 2190.
(17) Benson, S. W. *Thermochemical Kinetics*; Wiley: New York, 1968; Section 3.10.

then stored over 3A molecular sieves and transferred via syringe. Tris-(4-bromophenyl)amine and tris(4-bromophenyl)aminium hexachloroantimonate (both reagent grade) were used as obtained from Aldrich. *trans*-Anethole and 1,3-cyclohexadiene (also obtained from Aldrich) were distilled under N_2 and transferred by syringe. Reagent grade 2,4-dimethyl-1,3-pentadiene was also obtained from Aldrich and used as received. The various additives studied, viz., acetonitrile, diethyl ether, octanal, isopropyl alcohol, and triethylamine, were also commercial reagent grade chemicals, not further purified.

Apparatus. UV–visible spectra were obtained on a Hewlett-Packard 8450A diode array spectrophotometer equipped with a temperature controller and a thermostated cell holder. Cells were of 1-mm path length and were equipped with rubber septa for inert atmosphere work. The cell holder was also equipped with a nitrogen purge to inhibit water condensation on the cells. The 8450A spectrophotometer contains an internal software package for multicomponent analysis over any desired wavelength range from 200 to 800 nm. In addition, derivatized spectra are obtainable which minimize base-line shifts and maximize spectral resolution.

Kinetics Procedures. A typical kinetics experiment was carried out as follows. A 1-mm path-length cuvette with stopper was flame-dried under nitrogen. After cooling, 200 mL of a stock solution of 1,3-cyclohexadiene or *trans*-anethole (typically 2.0–4.0 × 10⁻³ M) was syringed into the cuvette. After a zero-time spectrum was taken, an aliquot of the aminium salt solution (usually 20 mol %) was syringed into the cuvette and mixed rapidly. Spectra were then recorded every 5–20 s, as required (depending upon the concentrations and the temperature). The spectra actually stored for each point consisted of two 1-s spectra, averaged, derivatized, and stored in the computer memory. After a length of time corresponding to about 50% reaction or until the absorbances changed too slowly to obtain multicomponent analyses, the experiment was stopped and data workup commenced.

The multicomponent analysis required standard spectra of 1,3-cyclohexadiene (or *trans*-anethole), the triarylaminium salt, and the corresponding triarylamine. The cyclohexadiene dimer product is transparent in the 200–800-nm range, but a *trans*-anethole dimer standard was also employed where appropriate. These standard spectra were measured on freshly prepared solutions and stored in the computer memory for later use. Multicomponent analysis of each point of the kinetic run then provided the required concentrations of the substrate, catalyst, and the free amine, along with a relative fit error for each component. Second-derivative spectra were utilized for both the standard solutions and the kinetic runs.

All conceivable rate laws corresponding to integral and/or half-integral substrate and catalyst concentration dependencies were carefully investigated in the search for a precise fit of the concentration time data. None gave a linear fit under all conditions except the ones proposed. The invariance of the rate law and rate constant thus obtained with respect to concentration variations was explored carefully at 25 °C. The cyclohexadiene concentration was varied between 3.5 × 10⁻³ and 7.0 × 10⁻⁴ M; *trans*-anethole between 4 × 10⁻⁴ and 9 × 10⁻⁴ M; the catalyst between 10 and 30 mol %. Under all of these conditions the proposed rate laws, and only the proposed rate laws, gave an excellent linear fit, and the rate constant was invariant within experimental error.

Temperature Dependence. Temperature control was accomplished by means of an HP89100A controller with HP8910A cell holder, which have a resolution of ±0.1 °C. The cuvette was placed in the cell holder after initial temperature bath equilibration and allowed to come to the equilibrium temperature. A dry N_2 stream blowing past the cell faces kept condensation from obscuring the cell face and adventitious water from working into the cell. The remainder of the kinetics experiment was carried out as previously. An Arrhenius plot (ln k vs. $1/T$) of the data was constructed using the average rate constants (up to 15 different measurements) at each temperature. Four different temperatures (0, 10, 17, 25 °C) were studied, constituting the widest possible range available in the study, as limited by the boiling point of the solvent (39 °C) and the limitations of the temperature controller (theoretically –10 °C).

Functional Group Compatibility. The compatibility of various functional groups with the aminium salt initiated cycloaddition was evaluated by carrying out kinetic studies, exactly as described above, on reactions containing 100 mol % (relative to 1,3-cyclohexadiene) of the following compounds: acetonitrile, diethyl ether, octanal, triethylamine, and isopropyl alcohol. These experiments were all carried out at 25 °C in the 3.5 × 10⁻³ M 1,3-cyclohexadiene (initially) and 20 mol % of the aminium salt.

Inhibition by the Triarylamine. Analogous rate studies were carried out for cyclodimerization reactions containing the neutral triarylamine. As is noted in Table II, rate retardation is substantial in both reactions, but is especially powerful in the cyclohexadiene case, where addition of 100 mol % of the amine nearly completely suppresses the reaction. In

the instances noted in the table, it was verified that the rate law remained unaffected by the added triarylamine.

Peak Potential Measurements. These potentials were measured on a BAS-100 electrochemical analyzer by Mr. Gary M. Reitz, whom we warmly thank for these experiments. The solvent was dichloromethane, the working electrode a Pt disk, the auxiliary a Pt wire, and the reference electrode Ag/0.1 M AgNO₃ in acetonitrile. The potentials were referenced to that of ferrocene and thence converted to the SCE reference.

Product Studies. The reactions studied here have been previously reported. Authentic samples of the cyclohexadiene Diels–Alder dimers were obtained by both thermal[18] and cation-radical dimerization routes. The identity of the products of the kinetic studies with the known cyclodimers was established by GC MS and GC spiking. The 95% yield quoted in the cyclohexadiene dimerization is a GC yield corrected by the appropriate response factor. The low concentrations involved in the kinetic runs, of course, precluded obtention of precise isolated yields.

Endo and Exo Diels–Alder Dimers of 1,3-Cyclohexadiene. To a solution of 1.061 g (13.2 mmol) of 1,3-cyclohexadiene (**1**) (Aldrich) in 40 mL of dry dichloromethane at 0 °C was added 0.641 g (0.785 mmol, 5.93 mol %) of the triarylaminium salt (**2⁺·**). The reaction was quenched after 5 min by the addition of excess sodium methoxide/methanol; the dichloromethane/methanol solution was extracted three times with water and twice with saturated brine. After drying over magnesium sulfate for 2 h, the solvent was removed by rotary evaporation. The (corrected) GC yield of the dimers was determined to be 71.3%. Samples of the endo/exo mixture for GC MS and NMR analysis were collected by preparative GC and compared (GC MS, NMR) to authentic samples of this mixture prepared by the thermal dimerization:[18] mass spectrum m/e 160 (M), 80 (B = base peak); ¹H NMR (CDCl₃) δ 6.28 (q, 2 H, exo), 6.15 (q, 2 H, endo), 5.8–5.4 (m, endo + exo), 2.5–0.9 (m, 12 H, endo + exo); ¹³C NMR (CDCl₃) (endo) 132.3, 133.9, 133.2, 128.1, 27.6, 40.7, 35.9, 37.9, 26.7, 25.8, 37.3, 23.„; (exo) 134.6, 135.8, 132.1, 130.2, 26.1, 40.5, 37.0, 33.4, 25.2, 21.4, 35.6, 18.8.

Trans,Anti,Trans Dimer of *trans*-Anethole. To a solution of 1.011 g (6.824 mmol) of *trans*-anethole (**3**) in 30 mL of dry dichloromethane at 0 °C was added 0.279 g (0.341 mmol) of 5.0 mol % of the triarylaminium salt (**2⁺·**). The blue color of **2⁺·** rapidly changed to brown. A single peak was observed (GC) to form in 43% (corrected GC) yield in less than 10 min. The reaction mixture was then quenched with methoxide/methanol solution and poured into a separatory funnel with excess dichloromethane. The organic phase was then extracted three times with water, dried, and concentrated in vacuo. The crude product was dissolved in 5 mL of dichloromethane and then slurried with 4 g of silica gel (EM Reagents) and evaporated to a fine powder. Silica gel column chromatography yielded, first, the triarylamine (R_f 0.21, hexane) followed by the product dimer (R_f 0.29, hexane/ethyl acetate (9:1)). The isolated yield of colorless oil was 0.435 g (43%): mass spectrum m/e 296 (M), 148 (B); ¹H NMR (CDCl₃) δ 7.2–6.7 (AA′BB′, 8 H, aromatic), 3.7 (s, 6 H, OMe), 2.77 (d, 2 H, benzylic), 2.0–1.6 (m, 2 H, methine), 1.15 (d, 6 H, CH₃). Decoupling also confirmed the structure assignment. ¹³C NMR (CDCl₃) 158.1, 136.0, 127.8, 113.8, 55.2, 52.7, 43.3, 18.9.

The ¹H NMR data are very similar to those found for the *trans,anti,trans*-β-methylstyrene dimer[19] and differ from those for the *trans,syn,trans* dimer of *trans*-anethole.[19]

Appendix

The rate is styled as:

$$\text{rate} = -d[1]/dt = k_p[1][1^{\cdot+}] + k_{CH}[1][D^{\cdot+}] = 2k_p[1][1^{\cdot+}] \tag{1}$$

Steady-state equations involving both $[1^{\cdot+}]$ and $[D^{\cdot+}]$ are then written:

$$d[1^{\cdot+}]/dt = 0 = k_i[1][2^{\cdot+}] - k_{-1}[1^{\cdot+}][2] - 2k_t[1^{\cdot+}]^2 - k_p[1][1^{\cdot+}] + k_{CH}[D^{\cdot+}][1] \tag{2}$$

$$d[D^{\cdot+}]/dt = 0 = k_p[1^{\cdot+}][1] - k_{CH}[D^{\cdot+}][1] \tag{3}$$

(18) Valentine, D.; Turro, N. J., Jr.; Hammond, G. S. *J. Am. Chem. Soc.* **1964**, *86*, 5202.

(19) Nozaki, H.; Otani, I.; Noyori, R.; Kawanishi, M. *Tetrahedron Lett.* **1968**, *24*, 2183.

From eq 3, [D$^{\bullet+}$] is obtained:

$$[D^{\bullet+}] = (k_p/k_{CH})[1^{\bullet+}] \qquad (4)$$

and substituting (4) into (2):

$$0 = k_i[1][2^{\bullet+}] - k_{-i}[1^{\bullet+}][2] - 2k_t[1^{\bullet+}]^2 \qquad (5)$$

The quadratic in [1$^{\bullet+}$] is easily solved, but the expression for [1$^{\bullet+}$] and thus the kinetic rate law has a simple form only if [2] is small:

$$[1^{\bullet+}] = (8k_ik_t[1][2^{\bullet+}])^{1/2}/4k_t \qquad (6)$$

Substituting (6) into (1):

$$\text{rate} = -d[1]/dt = \sqrt{2}(k_pk_i^{1/2}k_t^{-1/2})[1]^{3/2}[2^{\bullet+}]^{1/2} \qquad (7)$$

The analogous rate equation for the cyclodimerization of **3** is:

$$\text{rate} = -d[3]/dt = (k_pk_ik_t'^{-1})[3]^2[2^{\bullet+}]$$

The integrated rate equation corresponding to the rate law derived for the cyclodimerization of **1** and assuming [Ar$_3$N$^{\bullet+}$] constant is

$$2([1]_t^{-1/2} - [1]_0^{-1/2})([2^{\bullet+}])^{-1/2} = k_{app}t$$

Plots of:

$$2([1]_t^{-1/2} - [1]_0^{-1/2})([2^{\bullet+}])^{-1/2}$$

vs. *t* yielded the rate constants, k_{app}, given in Table I. These plots maintained excellent linearity with varying [1], [2], and temperature. Plots which were first or second order with respect to [1] or those which were other than one-half order in [2$^{\bullet+}$] were found unsatisfactory.

The integrated rate equation which fit the data for the dimerization of **3** is:

$$([3]_t^{-1} - [3]_0^{-1})[2^{\bullet+}]^{-1} = k_{app}t$$

Activation parameters were obtained in the usual way. The plots of ln k_{app} vs. T^{-1} had the following characteristics. For **1**, $r = -0.9952$, $y = 16.887$, $s = -4283.77$; for **3**, $r = -0.9965$, $y = $

15.3887, $s = -1358.37$. Arrhenius analysis gave for **1**, $E_a = 8.512$, $A = 2.16 \times 10^7$; for **3**, $E_a = 2.699$, $A = 4.822 \times 10^6$.

The separation of the $\Delta G^{\ddagger}_{app}$ into $\Delta G^{\ddagger}_p$ follows from the derivation below:

$$k_{app} = \sqrt{2}(k_pk_i^{1/2}k_t^{-1/2})$$

$$\Delta G^{\ddagger}_{app} = -RT \ln k_{app} =$$
$$-RT[\ln \sqrt{2} + \ln k_p + \tfrac{1}{2} \ln k_i - \tfrac{1}{2} \ln k_t]$$

$$\Delta G^{\ddagger}_{app} = \Delta G^{\ddagger}_p + \tfrac{1}{2}\Delta G^{\ddagger}_i - \tfrac{1}{2}\Delta G^{\ddagger}_t - RT \ln \sqrt{2}$$

$$\Delta G^{\ddagger}_p = \Delta G^{\ddagger}_{app} - \tfrac{1}{2}\Delta G^{\ddagger}_i + RT \ln \sqrt{2}$$

The preceding equation assumes the activation energy for termination (e.g., coupling) is negligible. The remainder of the separation into $\Delta H^{\ddagger}_p$ and $\Delta S^{\ddagger}_p$ is as follows:

$$\Delta H^{\ddagger}_p - T\Delta S^{\ddagger}_p =$$
$$\Delta H^{\ddagger}_{app} - T\Delta S^{\ddagger}_{app} - \tfrac{1}{2}(\Delta H^{\ddagger}_i - T\Delta S^{\ddagger}_i) + RT \ln \sqrt{2}$$

$$\Delta H^{\ddagger}_p = \Delta H^{\ddagger}_{app} - \tfrac{1}{2}\Delta H^{\ddagger}_i; \; -T\Delta S^{\ddagger}_p =$$
$$-T\Delta S^{\ddagger}_{app} + \tfrac{1}{2}T\Delta S^{\ddagger}_i + RT \ln \sqrt{2}$$

Finally, $\Delta H^{\ddagger}_i = \Delta G^{\ddagger}_i = \Delta E_p$ is assumed. That $\Delta S^{\ddagger}_i = 0$ is a reasonable approximation follows from the nature of the ionization equilibrium, which involves one cation radical and one neutral species on both reactant and products sides. The quantity ΔE_p is the difference in peak oxidation potentials of **1** and **2**, measured by cyclic voltammetry. Reversible potentials are not attainable, so that ΔE_p is not a true thermodynamic quantity. The potentials measured for **1** and **2**, respectively, are 1.60 and 1.05 V ($\Delta E_p = 0.55$ eV = 12.68 kcal mol^{-1}).

Synthesis and Claisen Rearrangement of Alkoxyallyl Enol Ethers. Evidence for a Dipolar Transition State

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Abstract: The synthesis and Claisen rearrangement of a series of 4-, 5-, and 6-alkoxyallyl vinyl ethers are reported. The 4- and 6-alkoxy derivatives (**4a–d, 13,** and **15**) rearrange 9.5–159 times faster than the parent allyl vinyl ethers. In addition, a significant solvent effect is observed; the rates of rearrangement of the 4- and 6-alkoxy derivatives are increased 18–68-fold upon changing from benzene to methanol, ethanol, or 80% aqueous ethanol while the parent allyl vinyl ethers show a much smaller solvent effect. Further acceleration of the rearrangements from the combined influence of a 4-alkoxy group and a cyano or carbethoxy group at C-1 indicates a synergistic interaction of the donor and acceptor substituents. The substituent and solvent effects provide experimental evidence for a pronounced dipolar character of the transition state. 5-Methoxyallyl vinyl ether (**14**) rearranges 40 times slower than allyl vinyl ether itself. This contrasts with the results of a MNDO theoretical treatment by Dewar which predicted a 2-oxacyclohexane-1,4-diyl-like transition state and acceleration from the 5-methoxy substituent.

The Claisen rearrangement of allyl vinyl ethers (**1 → 2**)³ and allyl aryl ethers is an important synthetic reaction for carbon–carbon bond formation⁴ and a pericyclic transformation of considerable mechanistic interest.⁵⁻⁸ Although the tolerance of the
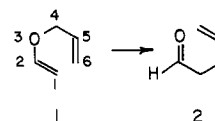
aliphatic Claisen rearrangement to various types of substituents has been amply demonstrated, the extent of quantitative infor-

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