(19) I. D. Entwistle and R. A. W. Johnstone, *J. Chem. Soc. C*, 1818 (1968).
(20) D. S. McClure, *J. Chem. Phys.*, **22**, 1668 (1954); **24**, 1 (1956); H. Zimmermann and N. Joop, *Z. Elektrochem.*, **64**, 1215 (1960).
(21) H.-G. Kuball and W. Euing, *Chem. Phys. Lett.*, **30**, 457 (1975).
(22) V. Dvořák, A. Manzara, and J. Michl, unpublished results.
(23) R. S. Becker, I. S. Singh, and E. A. Jackson, *J. Chem. Phys.*, **38**, 2144 (1963); J. L. Patenaude, P. Sauvageau, and C. Sandorfy, *Spectrochim. Acta*, **18**, 241 (1962), and references therein.
(24) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953); J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).
(25) A. W. Hanson, *Acta Crystallogr.*, **13**, 215 (1960).
(26) N. Mataga and K. Nishimoto, *Z. Phys. Chem.* (*Frankfurt am Main*), **13**, 140 (1957).
(27) J. Koutecký, J. Paldus, and R. Zahradník, *J. Chem. Phys.*, **36**, 3129 (1962).
(28) (a) J. F. Muller, D. Cagniant, O. Chalvet, D. Lavalette, J. Kolc, and J. Michl, *J. Am. Chem. Soc.*, **96**, 5038 (1974); (b) J. Kolc, E. W. Thulstrup, and J. Michl, *Ibid.*, **96**, 7188 (1974); E. W. Thulstrup, P. L. Case, and J. Michl, *Chem. Phys.*, **6**, 410 (1974); E. W. Thulstrup, J. Michl, and C. Jutz, *J. Chem. Soc., Faraday Trans. 2*, **71**, 1618 (1975); J. Kolc and J. Michl, *J. Mol. Spectrosc.*, **51**, 298 (1974); V. Kratochvil, J. Kolc, and J. Michl, *Ibid.*, **57**, 436 (1975).
(29) M. J. S. Dewar and N. L. Hojvat (Sabelli), *J. Chem. Phys.*, **34**, 1232 (1961); *Proc. R. Soc. London, Ser. A*, **264**, 431 (1961); K. Ohno, *Theor. Chim. Acta*, **2**, 219 (1964); G. Klopman, *J. Am. Chem. Soc.*, **86**, 4550 (1964).
(30) P. Hochmann, R. Zahradník, and V. Kvasnicka, *Collect. Czech. Chem. Commun.*, **33**, 3478 (1968).
(31) J. W. Downing, J. Michl, P. Jorgensen, and E. W. Thulstrup, *Theor. Chim. Acta*, **32**, 203 (1974).
(32) J. W. Downing, Ph.D. Dissertation, University of Utah, 1974; J. W. Downing and J. Michl, unpublished results.
(33) J. Karwowski, *Chem. Phys. Lett.*, **18**, 47 (1973).
(34) J. Cizek, J. Paldus, and I. Hubač, *Int. J. Quantum Chem.*, **8**, 951 (1974).
(35) H. C. Longuet-Higgins and R. G. Sowden, *J. Chem. Soc.*, 1404 (1952); C. A. Coulson, *Proc. Phys. Soc., London, Sect. A.*, **65**, 933 (1952).

Ionization Potentials, Electron Affinities, and Reactivities of Cyanoalkenes and Related Electron-Deficient Alkenes. A Frontier Molecular Orbital Treatment of Cyanoalkene Reactivities in Cycloaddition, Electrophilic, Nucleophilic, and Radical Reactions

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Abstract: The He(I) photoelectron spectra of nine cyanoalkenes (acrylonitrile, α-methylacrylonitrile, crotononitrile, vinylidene cyanide, tetracyanoethylene, 1,2-bis(trifluoromethyl)fumaronitrile, methyl α-cyanoacrylate, α-acetoxyacrylonitrile, α-chloroacrylonitrile) and two models (vinyl acetate and isopropenyl acetate) are reported. The experimental ionization potentials of these compounds and of fumaronitrile and maleonitrile have been used to estimate electron affinities of all the cyanoalkenes. The electron affinities calculated in this way correlate with other theoretical and experimental electron affinity estimates. The nature of the cyano substituent effect on π orbital energies is discussed, and correlations between frontier orbital stabilization energies and rates of Diels–Alder reactions (measured by Sauer et al.) are demonstrated. Whereas these reactions involve the partial formation of two bonds in the transition state, attack on cyanoalkenes by simple nucleophiles will involve formation of only one bond in the transition state. The calculated relative reactivities of cyanoalkenes toward "two-bond" nucleophiles is markedly different from the calculated relative reactivities with "one-bond" nucleophiles. The "one-bond" reactivities are in agreement with the available qualitative data on reactions of cyanoalkenes with nucleophiles such as amines and water. "One-bond" and "two-bond" nucleophilicities of cyanoalkenes are approximately the same. These reactivity indexes are also of use in the prediction of rates of radical addition to, and excited state quenching by, cyanoalkenes.

Introduction

Substituent effects on chemical reactivity are valuable probes of reactivity. Quantification of substituent effects in organic reactions has been achieved with varying degrees of success through use of Hammett- or Taft-type relationships, where rates or equilibria of standard reactions are used to define the magnitude and mechanism of electron withdrawal or release by substituents. Photoelectron spectroscopy provides a physical means to evaluate substituent effects, where the reference process is ionization of the neutral molecule. A comparison of the vertical ionization potentials (IP) of an unsubstituted molecule with a substituted molecule gives a direct measure of the influence of the substituent on the relative energies of the ground state and the radical cation in the ground state geometry. In the context of a charge-transfer (CT) or configuration interaction (CI) model of reactivity,[1-3] the IP's and electron affinities (EA) of molecules are partial indexes to the reactivity of a molecule with electrophiles, or with nucleophiles, respectively. Thus, changes in IP's (EA's) of molecules induced by substituents are not only valuable measures of substituent effects, but will have a direct relationship to the reactivity of a molecule.

Frontier molecular orbital treatments of reactivity,[1,2] in which the energies and shapes of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of a molecule dictate the reactivity of that molecule toward electrophiles or nucleophiles, respectively, provide a useful, if not rigorous, language in which to discuss chemical reactivity. Frontier molecular orbital treatments are a first approximation to a complete perturbation treatment of chemical reactivity.[1,2,4-6] By application of Koopmans' theorem,[7] where the negatives of the SCF orbital energies of a molecule are equated to the IP's of the molecule, the frontier molecular orbital method becomes equivalent to the CT or CI models of reactivity.[2] Furthermore, the use of orbital language is so convenient that it outweighs the opprobrium heaped by referees on those who pretend that orbitals, rather than states, have any reality.

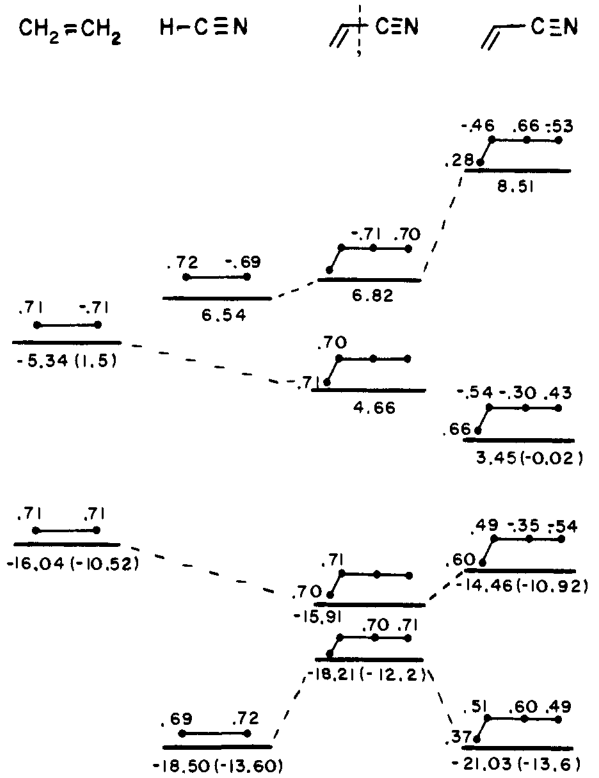

Figure 1. CNDO/2 calculations on ethylene, HCN, and acrylonitrile without and with π conjugation. The coefficients of π orbitals are given above the line, and calculated orbital energies and experimental IP's (in parentheses) are given below the lines.

In this paper, we wish to report photoelectron spectra of a series of cyanoalkenes and related molecules, to show how EA's of these molecules can be estimated, and to show nearly quantitative correlations between rates of reactions of the cyanoalkenes and calculated reactivities based on computed reactivity indexes. In addition, a new criterion for the mechanism of cycloadditions is proposed, based on the different reactivities of cyanoalkenes toward nucleophilic reagents which form one bond or two bonds in the rate-determining step of the reaction.

A Model of the Cyano Substituent Effect. Relative to hydrogen, the cyano group is both "inductively" electron withdrawing owing to its N and sp-hybridized carbon, and is conjugating owing to the presence of the π system. Substitution of a cyano group for a hydrogen in ethylene will lead to a lowering of the energies of the π and π^* orbitals of the vinyl group because of the "inductive" effect and to further energy changes due to conjugation of the vinyl and cyano π systems. One way to probe the relative magnitudes of these effects is through calculations with various matrix elements deleted.[8] Figure 1 shows CNDO/2 calculations for ethylene, hydrogen cyanide, acrylonitrile with the deletion of all the π matrix elements between the vinyl and cyano moieties, and acrylonitrile with all interactions included. The coefficients are calculated, but the energy scale used is experimental as far as possible. Union of the cyano and vinyl groups results in a lowering of the orbital energies of both groups due to "inductive" effects, while inclusion of conjugation causes mixing of both the filled π orbitals and the vacant π orbitals of the two moieties. The energy changes which occur upon including conjugation indicate some mixing of the vinyl HOMO with the cyano LUMO. The coefficient changes are particularly revealing. As noted in our earlier discussions of the HOMO coefficients in electron-deficient alkenes,[2,6] the "inductive effect" of the electron-withdrawing group polarizes the orbitals in the direction expected (cf. the π system of formaldehyde), while conjugation increases the ethylene LUMO polarization and reverses the HOMO polarization. The coefficients show that 55% of the acrylonitrile HOMO density resides on the vinyl moiety, while 73% of the LUMO density is on the vinyl moiety.

Photoelectron Spectra

The photoelectron spectra (PES) reported here were recorded on a Perkin-Elmer PS-18 photoelectron spectrometer with a He(I) source, using xenon and argon as internal calibrants. Resolution was 20–30 MeV in every case.

The photoelectron spectral data for the cyanoalkenes studied here [acrylonitrile, α-methylacrylonitrile, *trans*-crotononitrile, vinylidene cyanide (1,1-dicyanoethylene), tetracyanoethylene, 1,2-bis(trifluoromethyl)fumaronitrile, methyl α-cyanoacrylate, α-acetoxyacrylonitrile, and α-chloroacrylonitrile] are reported in Table I. Table I also lists ionization potentials of several cyanoalkenes (acrylonitrile,[9] fumaronitrile,[10] maleonitrile,[10] cyanoacetylene,[11] and dicyanoacetylene[11]), studied by others and IP's of several model compounds (ethylene,[11] acetylene,[11] acetonitrile,[9,12] methyl acrylate,[13] and vinyl chloride[44]), reported earlier in the literature. The table also lists data for vinyl acetate and isopropenyl acetate, model compounds whose PES we report here for the first time. The vertical ionization potentials listed are the maxima of each band.

The simply cyanoalkenes show rich vibrational structure which aid in the assignments. As shown in Table I, both C=C stretching and C≡N stretching vibrations are excited in each of the lowest ionizations, consistent with the loss of an electron from a π level which is traditionally identified as "π_{CC}" even though it is an orbital delocalized over both the alkene and cyano groups as shown in Figure 1.

The second band in these compounds is assigned to an orbital localized mainly on the CN moiety, as evidenced by the CN stretching mode observed in the vibrational structure. The orbital involved in this ionization is labeled π'_{CN} and is an in-plane orbital which has its origin in one of the degenerate π_{CN} orbitals of HCN. In the polycyanoalkenes, there are several "π'_{CN}" orbitals which, because of through-bond coupling, are not degenerate.[10]

The third band (or group of bands in the polycyano compounds) is due to ionizations from the "n_{CN}" orbital. This is an orbital identified with the sp hybrid lone pair on nitrogen or, in molecular orbital terms, with a σ orbital mainly localized on nitrogen.[12]

With tetracyanoethylene, a number of maxima are observed in the region in which four n_{CN} and four π'_{CN} ionizations are expected. We have not attempted to decipher this region of the spectrum but list the maxima observed. The assignments for the cyanoalkenes and cyanoalkynes[11] are correlated in Figure 2.

Turning to the compounds containing both nitrile and ester functions, assignments must be made mainly on the basis of model compounds. The correlations deduced in this way are shown in Figures 3 and 4. The assignments for methyl acrylate were made by Sustmann and Trill,[13] while those for the enol acetates have not been reported previously. Since vibrational structure is absent in the spectra of those compounds, correlations between methyl acetate ($I_v(n_{CO})$ = 10.59 eV)[13] and ethylene ($I_v(\pi_{CC})$ = 10.52 eV)[11] were used to assign the vinyl acetate I_v's at 9.85 and 10.75 eV to π_{CC} and n_{CO} ionizations, respectively. That is, the vinyl group is electron withdrawing with respect to the methyl group, so that the n_{CO} orbital of methyl acetate should be inductively stabilized by vinyl substitution. The π_{CC} orbital, by contrast, should be destabilized by acetoxy substitution.

Table I. Vertical Ionization Potentials (±0.05 eV), Vibrational Structure (±400 cm^{-1}), and Band Assignments in Photoelectron Spectra of Cyanoalkenes

Cyanoalkenes and models	π_{CC}	π'_{CN}	n_{CN}	Other	Ref	EA (calcd)
Ethylene	10.52 (1230, 430, 1340)				11	−1.3
Acetonitrile		12.20 (2010, 800)	13.14 (1370)	14.11–15.62	9	
		12.18 (1925, 900)	13.11 (1360)	15.15	12	
Acrylonitrile	10.92 (1226, 1395, 2081)	12.35 (1820)	13.00		This work	0.02
	10.91 (1450, 2000)	12.36 (2000, 1100)	13.04 (100)		9	
α-Methylacrylonitrile	10.37 (1390)	12.11 (1860)	12.82 (1300)	~13.2	This work	
Crotononitrile	10.23 (1410, 850)	12.04 (1830)	12.89	~13.4	This work	
Maleonitrile	11.15 (2080, 1440)	12.77 (1960) 13.35	~13.5	14.30 (2160, 800, 400) −π; 15.75, 17.4, 19.1	10	0.78
Fumaronitrile	11.15 (2160, 1360)	12.78 (2160, 640) 13.10 (480)	13.44 (880)	13.67 (2080, 960) − π; 14.41 (2160, 480) − π; 15.62; 18.2; 19.7	10	0.78
Vinylidene cyanide	11.38 (1250, 2140) ~13.1	12.97	13.25 (1370)	13.67; 1390	This work	1.54
Tricyanoethylene	11.55 (estd; see text)				This work	2.10
Tetracyanoethylene	11.79 (1250, 2130)	13.45 (1950), 13.80, 13.93, 14.05, 14.23, 14.45, 14.64, 14.81			This work	2.88
trans-1,2-Bis(trifluoromethyl)-fumaronitrile	11.85 (1210, 1500)	13.14 (690) 13.63	13.84 (890) 14.06 (890)	14.81		

Compound	π_{CC}	n_{CO}	π'_{CN}	n_{OMe}	n_{CN}	Other	Ref
Acrylic esters							
Methyl α-cyanoacrylate	10.98 (1290, 2400)	11.62	12.56		13.03 (1450)	14.48	This work
Methyl acrylate	10.72	11.12					13
α-Acetoxyacrylonitrile	10.76	11.23					This work
Vinyl acetate	9.85	10.73		12.60			This work
Isopropenyl acetate	9.74	10.52		11.36			
Cyanoalkynes and models							
Acetylene	11.40						11
Cyanoacetylene	11.60		13.54	14.03			11
Dicyanoacetylene	11.81		13.89 (3 bands?)	14.95			11
Vinyl chlorides		n_{Cl}					
α-Chloroacrylonitrile	10.58 (1390)	12.27	12.70 (2010)		13.40		This work
Vinyl chloride	10.15 (1290, 800)	11.61				13.07	44

The 0.67 eV destabilization of the vinyl π orbital by acetoxy substitution should be compared with the 1.47-eV destabilization caused by methoxy substitution,[43] in accord with the weaker π donor ability of the acetoxy group as compared to a methoxy group. Methyl substitution on ethylene raises the π orbital energy by 0.78 eV,[11] so that the acetoxy group is a poorer donor than methyl, according to this measure.

The π ionization potential of α-chloroacrylonitrile (10.58 eV) is nearly the same as that of ethylene, since the chlorine lowers the IP, and the cyano group raises it to approximately the same extent.

Calculation of Electron Affinities from Ionization Potentials

The cyanoalkenes studied here are all more or less electrophilic species, and their reactivities will be dominated primarily by their lowest vacant orbital energies, which, by an extension of Koopmans' theorem,[7] can be equated to the negatives of the electron affinities of these compounds. In a perturbation treatment of cyanoalkene cycloadditions, or of reactions of nucleophiles with cyanoalkenes, the electron affinities of the cyanoalkenes are the quantities of interest. For reasons discussed later, we suspected that, in the cyanoalkenes, the ionization potentials and electron affinities might be linearly related.

This contention can be qualitatively justified in several ways. Since all of the hydrocarbon analogues of ethylene through tetracyanoethylene are alternate hydrocarbons, in a one-electron (Hückel) treatment, the raising of the HOMO energy and lowering of the LUMO energy by substitution along the series will be identical. If one then considers substitution of one or more nitrogens for carbons in these systems, both the LUMO and the HOMO will be lowered to the same extent, because the coefficients at a single position will be the same in the HOMO and LUMO of an alternate hydrocarbon. Thus, the LUMO stabilization caused by both conjugation and substituent electronegativity will be greater than, but linearly related to, the HOMO energy change caused by conjugative destabilization and electronegativity stabilization. On a somewhat more sophisticated level, from the standpoint of substituent effects in a perturbation model, the LUMO and HOMO will both be

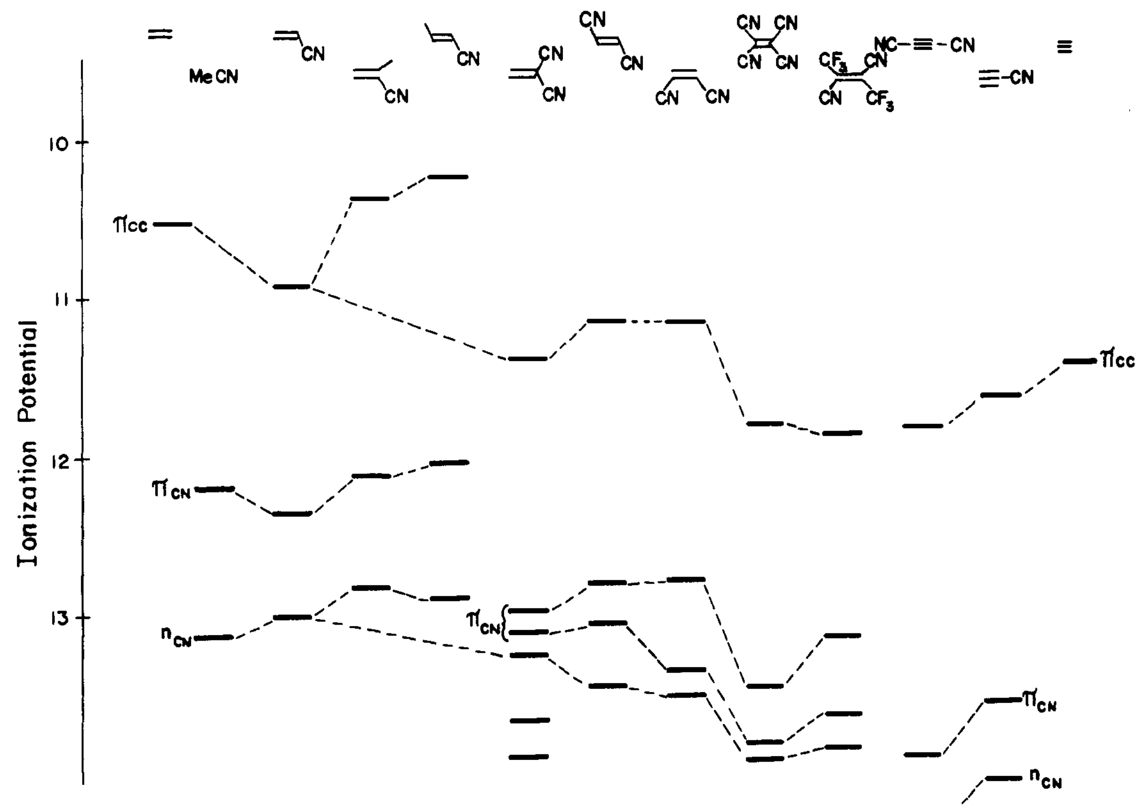

Figure 2. Correlations between ionization potentials of cyanoalkenes, cyanoalkynes, and nonconjugated models.

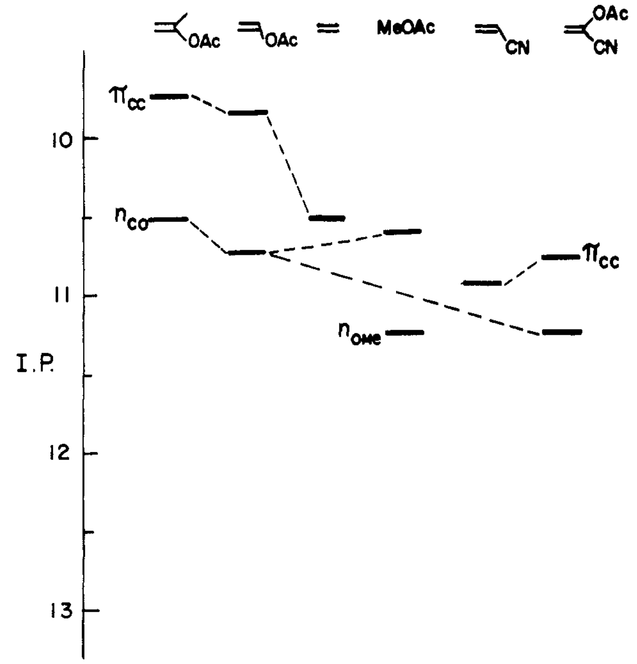

Figure 3. Correlations between ionization potentials of enol acetates.

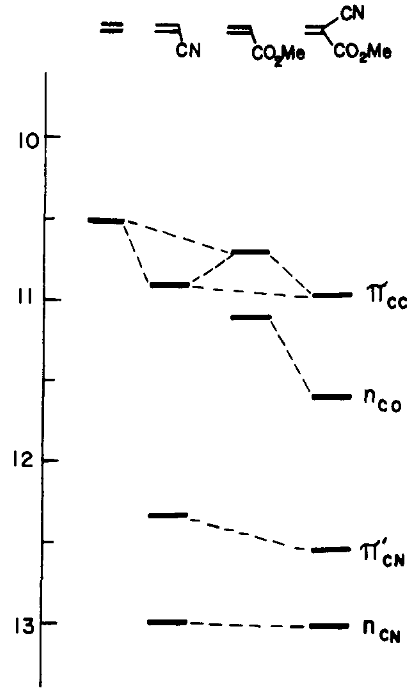

Figure 4. Correlations between ionization potentials of α-cyanoacrylate and several model compounds.

stabilized as a result of modification of the core potentials and electron repulsions resulting from mixing of σ orbitals on ethylene and the substituent. These parts of the HOMO and LUMO energy changes will be functionally related. Secondly, the conjugative change in energy of the frontier orbitals (stabilization of the LUMO, destabilization of the HOMO) depends on the difference in energy of ethylene and substituent π-systems. A functional relationship between the conjugative change is also expected. However, those qualitative considerations do not reveal whether the LUMO and HOMO changes will be linearly related, or will be related by some more complex functional relationship.

Although insufficient electron affinities are available to test this functional relationship directly, electron affinities have been measured by the magnetron technique for tetracyanoethylene (EA = 2.88 ± 0.06 eV) and fumaronitrile (EA = 0.78 ± 0.10 eV).[14] Using these values and the first vertical ionization potentials of fumaronitrile and tetracyanoethylene listed in Table I, the following equation can be derived (all energies in eV):

$$\mathrm{EA} = 3.3(\mathrm{IP}) - 36$$

This equation was used to calculate the electron affinities of the cyanoalkenes, and these are listed in the last column of Table I. Interestingly, this equation leads to a predicted electron affinity of −1.3 eV for ethylene, whereas a spectroscopic estimate of the EA of the vinyl group gives a value of −1.84 eV,[15] and ab initio calculations for the EA of ethylene give values ranging from −1.7 to −6.7 eV.[16] In our earlier treatment of 1,3-dipolar cycloadditions, we adopted the "reasonable" value of −1.5 eV.[6]

Professor Warren J. Hehre has recently informed us of the results of his ab initio STO-3G calculations on the cyanoalkenes.[17] These calculations give both a good account of ionization potentials ($I_v'(\text{exptl}) = 1.04 I_v'(\text{calcd}) + 1.46 \pm 0.06$ eV) and show a reasonable correlation between calculated HOMO energies and LUMO energies, with the change in LUMO energy about five times the change in HOMO energy. Thus, at the STO-3G level, the correlation between HOMO and LUMO energies and, assuming Koopmans' theorem, between IP and EA obtains for the cyanoalkenes. There is also a good correlation between the electron affinities estimated here and the reduction potentials of three cyanoalkenes. Such a relationship has been noted before in aromatic hydrocarbons.[18] Unfortunately, data are only available for acrylonitrile ($E_{1/2}(\text{H}_2\text{O}) = -1.84$ V),[19] fumaronitrile ($E_{1/2}(\text{H}_2\text{O}) = -1.28$ V),[20] maleonitrile ($E_{1/2}(\text{H}_2\text{O}) = -1.29$ V),[20] and tetracyanoethylene ($E_{1/2}(\text{MeCN}) = -0.16$ V),[21] so the extrapolation for tricyanoethylene and vinylidene cyanide cannot be tested. Using the known values, the following relationship is obtained:

$$E_{1/2}(\text{V}) = +0.59(\text{EA, eV}) - 1.80 \pm 0.06 \text{ V}$$

The predicted reduction potentials of vinylidene cyanide and tricyanoethylene are −0.89 and −0.56 V, respectively.

Although only two values of relevant charge-transfer transition energies are known to us, the energies of charge-transfer transitions for complexes of TCNE and tricyanoethylene with durene (2.5 and 3.40 eV, respectively)[22] also lend support to the calculated electron affinities. The difference in electron affinities of these acceptors should be related to the difference in CT transition energies (0.82 eV).[18] The corresponding EA difference is 0.78 eV according to our estimate.

Estimates of the TCNE EA from charge transfer spectra and reduction potentials have been summarized by Briegleb.[18] Values ranging from 1.5 to 2.2 eV, with an average of 1.8 eV, have been obtained in this way. Although these values are consistently smaller than the magnetron value used here, it is interesting that estimates of the EA of I_2 from charge-transfer spectra (1.0 − 2.0 eV)[18] are lower than recently determined gas-phase measurements of the EA of I_2 (2.42 ± 0.02 eV).[23] Thus, the value of the EA of TCNE used here (2.88 eV) is not unreasonably large.

Substituent Effects on Ionization Potentials and Electron Affinities

For the cyanoalkenes, including ethylene, there is an approximate correlation of the lowest ionization potential and the number of cyano groups (n) in the molecule:

$$\text{IP} = 10.52 + n(0.32 \text{ eV})$$

There is a slight curvature in this plot resulting from the gradual decrease in the effect of successive cyano groups, and the site of substitution is important as can be seen from a comparison of the IP's of 1,1- and 1,2-dicyanoethylenes. Since the EA's were calculated from IP's, there is a similar approximate relationship for the EA's:

$$\text{EA} = -1.3 + n(1.06 \text{ eV})$$

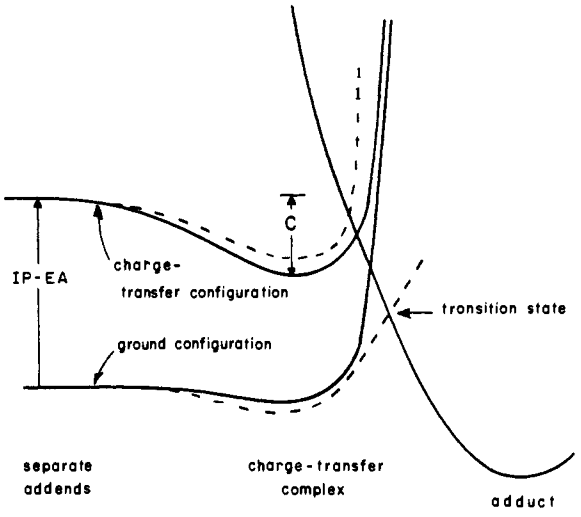

Figure 5. The CI model of Diels-Alder reactions.

The change in EA caused by cyano substitution is 3.3–3.5 times the change in IP. This is compatible with the model of the cyano substituent effect mentioned earlier: the inductive effect of the cyano group lowers both the HOMO and LUMO energies, but conjugation of the alkene and cyano π orbitals lowers the alkene LUMO energy, but raises the alkene HOMO energy.

Finally, the effect of methylation on the ionization potential of acrylonitrile is of interest. As can be seen in Table I, α-methylation of acrylonitrile produces a 0.55-eV decrease in IP, while trans-β-methylation produces a 0.69-eV decrease in IP. For comparison, α- and trans-β-methylation of methyl acrylate reduces the IP by 0.44 and 0.61 eV, respectively, while for acrolein, decreases of 0.47 and 0.79 eV are observed.[13] The trend is for a larger effect of β-methyl than of α-methyl substitution, which is compatible with the larger coefficient at the unsubstituted carbon in the HOMO.[6] That is, if the methyl substituent effect is hyperconjugative in nature, the larger effect will be felt at the site of the large π coefficient.

The cyano substituent effect is larger upon α-substitution (0.46 eV) of acrylonitrile than upon β-substitution (0.23 eV). This result can be rationalized if the "inductive" effect is less sensitive to the coefficient at the site of attachment than the conjugative effect.

Correlations between Ionization Potentials, Electron Affinities, and Reactivity

The CT, or CI, model of reactivity is represented in Figure 5.[2] The lowest curve represents the energy change attending union of the ground states of addends without "electronic relaxation," and the upper curve represents energy changes in various "charge-transfer" configurations. As the transition state geometry is approached, the ground and charge-transfer configurations get nearer in energy by an amount, C, and the extent of interaction increases, stabilizing the transition state. Higher energy charge-transfer configurations mix less extensively with the ground configuration owing to the greater difference between the energy of these configurations. The frontier orbital approximation is equivalent to the inclusion of only the lowest energy charge-transfer configuration in the estimate of transition state stabilization. The extent of interaction between the lowest CT configuration, or, equivalently, between the donor HOMO and the acceptor LUMO, in the transition state may be calculated according to the second-order perturbation expression:

$$\Delta E = \frac{(\Sigma C_A C_D)^2 \beta^2}{\mathrm{IP_D} - \mathrm{EA_A} - C}$$

The numerator of this equation is the square of the resonance integral which measures the extent of interaction between the HOMO of the donor reactant and the LUMO of the acceptor reactant. C_A and C_D are the frontier orbital coefficients of the acceptor and donor, respectively, at sites of interaction. C is the amount by which the charge-transfer configuration drops in energy as the molecules are brought from infinite separation to transition-state separation.

Adopting a simple Evans-Polanyi model for calculation of activation energies,[2,24] we assume that the activation energy in the absence of charge-transfer stabilization will be some constant, E_a^0, while stabilization by CT will lower the activation energy by an amount ΔE. Making this assumption, the activation energy and rate of reaction becomes:

$$E_a = E_a^0 - \Delta E$$

and

$$k = A^{-E_a/RT}$$

$$\ln k = \ln A - E_a/RT = \ln A - E_a^0/RT + \Delta E/RT$$

Assuming A and E_a^0 constant for a series of similar reactions, then $\ln k$ for the series of molecules should be linearly related to ΔE. Curvature in such a plot is expected if any of the following obtain: (1) C is not approximately a constant, indicating the position of the transition state and/or the Coulombic attraction in the CT configuration varies along the series; (2) E_a^0 is not a constant, indicating that closed-shell repulsion or steric effects, and/or bond and angle distortions are different in the series; (3) the "goodness" of the frontier orbital approximation varies along a series (vide infra).

A number of authors have noted that plots of cycloaddition rates vs. IP's or EA's of the varied addend show good correlations.[5,25-28] Linearity is not expected, except over a limited series, since ΔE is the quantity linearly related to $\ln k$, according to theory, and ΔE contains the term

$$[\mathrm{IP} - \mathrm{EA} - C]^{-1}$$

However, typical electrophiles have EA's of 1-2 eV, C will be in the range of 4-6 eV, and typical alkenes which undergo reactions with electrophiles have IP's of 8-11 eV. Over such a narrow range, a plot of rate vs. IP will be nearly as linear as a plot of $[\mathrm{IP} - \mathrm{EA} - C]^{-1}$.

Such plots of rate vs. IP are given in Figure 6 for the reactions of cyanoalkenes. The kinetic data on the Diels-Alder reactions of cyclopentadiene and 9,10-dimethylanthracene have been measured by Sauer and coworkers,[29] and, as the plots show, there is a remarkably good correlation between rates and cyanoalkene IP's. However, the cyanoalkenes are the electrophilic species in these Diels-Alder reactions, so a plot of rate vs. alkene EA would be more appropriate. As noted in previous sections, the IP and EA's of cyanoalkenes are nearly linearly related, so that Figure 6 is equivalent to a plot of rate vs. cyanoalkene EA. One notable feature of Figure 6 is that cyclopentadiene (CP) is more reactive than dimethylanthracene (DMA) with acrylonitrile, but the opposite order of reactivity is observed with TCNE. This, as well as the greater curvature of the DMA line, can be explained by taking into account the different IP's and coefficients of the CP and DMA HOMO's.

Some relevant data are given in Figure 7. The diene HOMO-cyanoalkene LUMO gaps are clearly smaller than the other frontier orbital pairs for all of these reactants.[30] Taking only the diene IP's into account would suggest that DMA should be more reactive than CP with all dienophiles. However, the HOMO coefficients of DMA are smaller than those of CP (CNDO/2 calculations give 0.439 and 0.573, respectively, at the diene termini), so that overlap will favor CP reactions. The numerator of the expression for ΔE contains a C_D^2 term, and this is 1.7 times larger for CP than for DMA. For the mildly electrophilic acrylonitrile, the denominators of the expression for ΔE are not greatly different, and CP is more reactive than DMA. If a value of 4 eV is chosen for C, $\Delta E(\mathrm{CP}) - \Delta E(\mathrm{DMA}) = 0.08$. As the dienophile becomes more electrophilic, the numerators of the ΔE's remain constant, but the denominator of ΔE for DMA decreases faster than for CP. Again using $C = 4$ eV, $\Delta E(\mathrm{CP}) - \Delta E(\mathrm{DMA}) = -1.37$ for TCNE. We have suggested the term "frontier-density controlled" for reactions such as the Diels-Alder reactions of acrylonitrile, because the diene HOMO electron density determines the more reactive diene and "frontier-energy controlled" for reactions like those of TCNE, where orbital energies control rates.[2b] Both of these are special cases of Klopman's "frontier-controlled" reactions,[4,34] and so the more descriptive terminology has been proposed.

Finally, log k vs. the calculated quantity, ΔE, is plotted in Figure 8. ΔE has been plotted using the IP's and EA's discussed in this paper, diene HOMO and cyanoalkene LUMO coefficients calculated according to the CNDO/2 method (vide infra),[34] and a C of 4 eV, which corresponds to the attraction of a plus and minus charge separated by 3.6 Å.

Eisenstein and Anh have also calculated ΔE for the reactions of cyclopentadienes with all cyanoalkenes, using the diene HOMO and dienophile LUMO energies and coefficients calculated by the Hückel method.[36] A plot of Anh's calculated ΔE show that 1,2-dicyanoethylenes are calculated to be more reactive, and 1,1-dicyanoethylene less reactive, than is observed experimentally, so there is a definite improvement in the use of experimental quantities in the calculations.

In Figure 8, the only systematic deviation from the line occurs for vinylidene cyanide, perhaps due to a slight overestimation of the EA of this species. The most remarkable feature of the plot is that, whereas the theoretically unjustifiable plot of rate vs. IP (Figure 6) is nearly linear, the plot vs. the theoretically meaningful ΔE (Figure 8) is decidedly nonlinear. The rates of reaction do not increase linearly with ΔE, but level off for the most reactive cyanoalkenes. A possible explanation of the lack of linearity in Figure 8 lies in the assumption that the transition states of all these reactions have nearly identical structures. The calculations of ΔE with β and C kept constant are equivalent to this assumption. In reality, the transition state may shift toward reactants in structure for the very reactive addend pairs. This could be taken into account by calculating β and C explicitly. We note here only that decreasing β and C as the IP − EA difference decreases or using a smaller value of C throughout would diminish the curvature in the plot. The lower reactivity of DMA vs. CP for a constant calculated ΔE could be attributed to steric effects, but because of the uncertainty in β and C in the transition state, this is not unequivocal. For example, C for DMA should be smaller than that for CP owing to the fact that a positive charge on DMA will be more diffuse than that on CP. Reducing the value of C for DMA to 3.14 eV would result in identical calculated reactivity of CP and DMA with TCNE.

A second source of nonlinearity arises from the frontier orbital approximation itself. For example, we have neglected the interaction of the diene HOMO-dienophile next to lowest unoccupied orbital (NLUMO), as well as the interaction of the cyanoalkene HOMO's with the diene

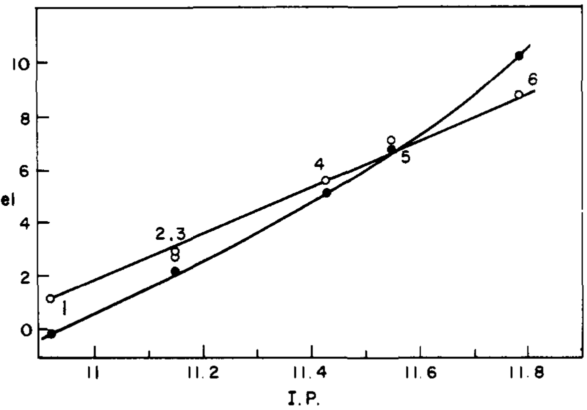

Figure 6. A plot of relative rates of Diels-Alder reactions of DMA (●) and CP (○) with (1) acrylonitrile, (2) vinylidene cyanide, (3) maleonitrile, (4) fumaronitrile, (5) tricyanoethylene, and (6) tetracyanoethylene vs. the ionization potential of the alkenes.

LUMO's.

To test the importance of "extra-frontier" interactions, calculations were performed using coefficients from Figure 1 for the acrylonitrile LUMO and NLUMO and estimated orbital energies of -0.02 and $+3.0$ eV for these orbitals, respectively, the CP energies shown in Figure 7, terminal coefficients of 0.57 and 0.49 for the CP HOMO and LUMO, respectively, and a C of 4 eV. For the CP-acrylonitrile pair, the CP HOMO-acrylonitrile LUMO interaction provides a stabilization energy of $\Delta E = 0.103\beta^2$, while the CP NHOMO-acrylonitrile NLUMO interaction gives a $\Delta E = 0.024\beta^2$, and the CP LUMO-acrylonitrile HOMO interaction gives $\Delta E = 0.036\beta^2$. Of the total stabilization provided by these three interactions, 63% results from the CP HOMO-acrylonitrile LUMO, and 15% from the CP LUMO-acrylonitrile HOMO interactions.

This calculation was performed for the most stringent test of the frontier MO theory of the cases discussed here. That is, as the EA of the cyanoalkene increases, the principal frontier MO interaction will become more dominant, and the diene LUMO-cyanoalkene HOMO interaction will rapidly diminish. Thus, part of the curvature in the plot results from the fact that the ΔE calculation is quite complete for TCNE and gives a smaller percentage of the total stabilization energy for acrylonitrile.

All of the foregoing discussion has been based on the premise that both new bonds which are formed in the reaction are partially formed to the same extent in the transition state. In fact, the frontier MO model can provide evidence in favor of the timing of the bond formation, as shown in the next section.

Nucleophilic Reactivity of Cyanoalkenes

In the frontier orbital treatment of nucleophilic additions to electrophilic alkenes, the EA of the alkene and the larger LUMO coefficient should be good indexes. That is, for "one-center" nucleophiles such as amines and hydroxide (as opposed to the "two-center" nucleophilic dienes discussed in the previous section), interaction between the nucleophile HOMO and alkene LUMO will facilitate reaction, and the transition state will be most stabilized when the nucleophile attacks at the site of largest alkene LUMO coefficient. Thus, ΔE for a nucleophilic reaction is:

$$\Delta E = \frac{(C_D C_A)^2 \beta^2}{\mathrm{IP}_D - \mathrm{EA}_A - C}$$

For the cyanoalkenes, the denominator of this equation is identical with that discussed in the last section, predicting the same order of reactivity. However, the numerator of the

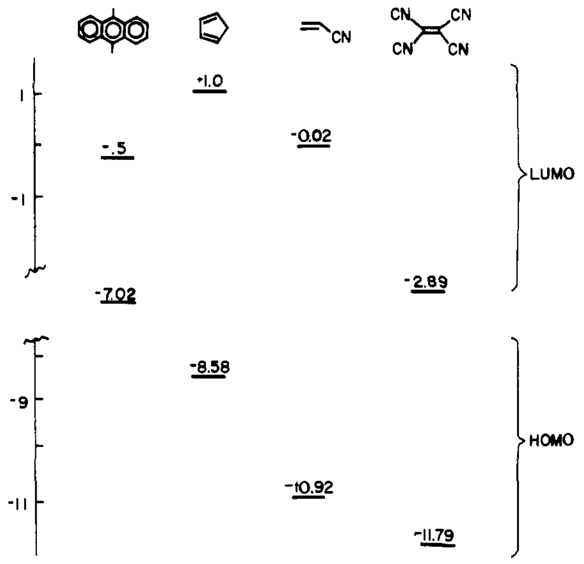

Figure 7. Frontier orbitals of DMA, CP, acrylonitrile, and TCNE.

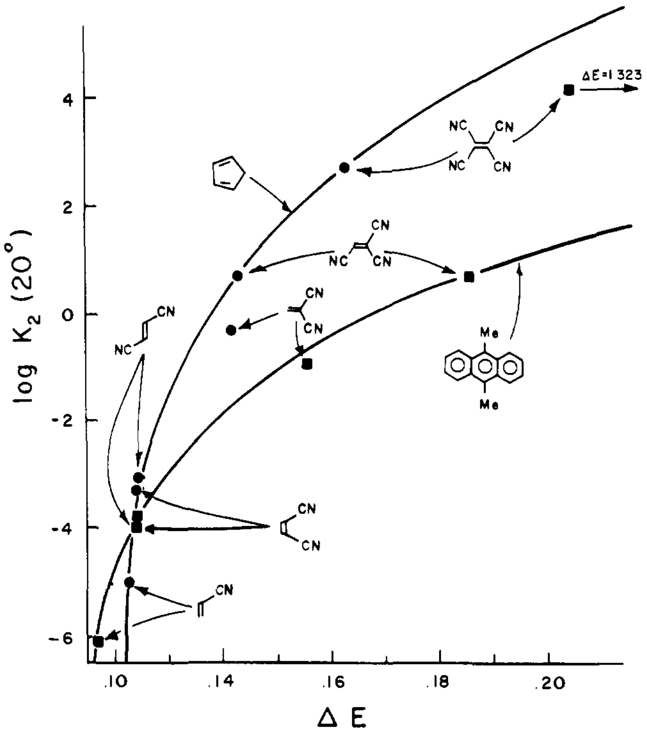

Figure 8. Plot of log k_{rel}[29] of Diels-Alder reactions of cyanoalkenes vs. ΔE (defined in text).

expression depends only the larger cyanoalkene LUMO coefficient.

Table II shows the CNDO/2 LUMO coefficients of the cyanoalkenes discussed so far. For the previously discussed series of cyanoalkenes, there is a remarkable regularity in coefficients, 0.66 for CH_2, 0.54-0.56 for CHCN, and 0.49 for $C(CN)_2$ positions. The result is that the term, $(C_L + C_S)^2$, used in calculations of Diels-Alder reactivity decreases monotonically as EA increases (as the LUMO becomes less ethylene-centered and more nitrile-centered) with the exception of vinylidene cyanide, which has larger LUMO coefficients than expected from its EA. In Diels-Alder reactions, the increase in reactivity caused by increasing EA is somewhat tempered by decreasing LUMO coefficients. The situation is markedly different for reactions with nucleophiles in which only one bond is partially formed in the transition state.

Table II. Properties of Cyanoalkene LUMO Coefficients and Calculated Cyanoalkene Electrophilicities

Cyanoalkene	C_L[a]	C_S[a]	EA	$(C_L + C_S)^2$	C_L^2	$C_L^2/12.6 -$ EA $- 4$	$C_L^2/8 -$ EA $- 4$
Acrylonitrile	0.66	0.54	0.02	1.44	0.44	0.051	0.109
Fumaronitrile	0.56	0.56	0.78	1.25	0.31	0.040	0.097
Maleonitrile	0.56	0.56	0.78	1.25	0.31	0.040	0.097
Vinylidene cyanide	0.66	0.49	1.54	1.32	0.44	0.062	0.177
Tricyanoethylene	0.56	0.49	2.10	1.10	0.31	0.048	0.165
Tetracyanoethylene	0.49	0.49	2.88	0.96	0.24	0.042	0.214

[a] These quantities are absolute values of the LUMO coefficients (CNDO/2); C_L is the larger coefficient and is always at the less substituted carbon; C_S is the smaller coefficient and is always at the more substituted carbon.

The quantity C_L^2 is considerably larger for the unsymmetrical species than for the symmetrical, and there is no semblance of monotonic behavior. As a result, the reactivities with "one-bond" nucleophilies and "two-bond" nucleophiles are different. Table II gives calculated reactivities for reactions of cyanoalkene with two model nucleophiles, one with an IP of 12.6 eV (water)[11] and the second with an IP of 8.0 eV, which is a typical value for tertiary amines.

The predicted order of reactivity for the model calculation, where IP = 12.6 eV, is 1,1-di- > 1- > tri- > tetra- > 1,2-dicyanoethylene, whereas with a nucleophile of IP = 8 eV, the order is tetra- > 1,1-di- > tri- > 1- > 1,2-dicyanoethylene. Depending on the IP of the nucleophile, the predicted orders of reactivity are different; the trend is toward "frontier-density control" with nucleophiles of high IP and "frontier-energy control" with nucleophiles of low IP. In neither extreme of calculated reactivity noted above is the order of reactivity calculated for two-bond cycloadditions observed, so that different behavior is expected depending on whether reactions are of the one-bond or two-bond type.

Unfortunately, we are aware of no quantitative data on the rates of addition of nucleophiles to cyanoalkenes. However, the calculated relative reactivities correspond rather well to qualitative experience. For example, vinylidene cyanide is extraordinarily reactive with nucleophiles, undergoing rapid polymerization in the presence of traces of water.[37] The calculations for IP = 12.6 eV predict acrylonitrile to be the next most reactive compound, whereas water and alcohols add readily to acrylonitrile only in the presence of basic catalysts.[37] The calculated reactivity of acrylonitrile appears too large, but the calculated reactivities are rather sensitive to the choice of C. Qualitatively, tricyanoethylene falls between vinylidene cyanide and tetracyanoethylene in reactivities with water or hydroxide,[22] as predicted in the first column of calculated reactivities in Table II. The calculated reactivities of fumaronitrile and maleonitrile are probably correct, since these compounds are relatively unreactive with weak nucleophiles.

The last column in Table II gives calculated reactivities for nucleophiles of low ionization potential. In this column, TCNE is predicted to be the most reactive, primarily due to the high EA of this compound which now overcomes the relatively small LUMO coefficients. Although little is known to verify or disprove the predicted order of reactivities, dimethylaniline reacts more rapidly with TCNE than with tricyanoethylene,[22] as predicted for nucleophiles with low ionization potentials. These reactions may very well involve electron transfer, since IP − EA − 4 eV for *N,N*-dimethylaniline-TCNE is only 0.56 eV, and nucleophiles with low ionization potentials (I^-, tertiary amines) are known to give the TCNE radical anion.[39]

Reactivity Criteria for Mechanisms of Cycloadditions

The considerations in the last two sections suggest a semiquantitative test for cycloaddition mechanisms. Figure 9 shows a plot of ΔE calculated for "two-bond" reactions such as concerted cycloadditions as a function of the nucleophilicity of the second species. For calibration purposes, IP − C = 6 eV corresponds to an IP of 10 eV for a C of 4 eV. Although typical Diels-Alder dienes have much lower IP's, many 1,3-dipoles and "electron-deficient" dienes have IP's in this range. The ΔE's indicate little selectivity in cycloaddition rates with the different cyanoalkenes for very weakly nucleophilic species. As the nucleophilicity of the diene increases, the reactivity of all the species increases, and the reactivity becomes the same as the order of EA's for normal ranges of diene IP's (IP < 8.5 eV).

By contrast, the "one-bond" electrophilicities shown in Figure 10 show entirely different orders for all nucleophiles. For reasonable nucleophile IP's of 7-10 eV (IP − C = 3-7 eV) the decreasing order of reactivity is: 1,1-di- > tri- > 1- > 1,2-dicyanoethylene, with TCNE varying from most reactive with nucleophiles of low IP, to intermediate in reactivity with higher nucleophile IP's.

Up to now, all reactions have been discussed in terms of frontier orbital interactions or CI with the lowest CT state. In order to show that this is a good approximation, we consider briefly how considerations of other orbital interactions will modify the calculated reactivities, if at all. As noted earlier, the inclusion of only the diene HOMO-cyanoalkene LUMO interactions neglects certain interactions which will be of more importance for the moderately electrophilic alkenes than for the strongly electrophilic ones. Similar calculations using a model nucleophile of IP = 9 eV and C = 4 eV show that for acrylonitrile, interaction of the nucleophile HOMO with the acrylonitrile NLUMO contributes only 10% as much stabilization as the HOMO-LUMO interaction. Furthermore, for usual one-bond nucleophiles, no relatively low-lying LUMO's of the proper symmetry will be present to give added stabilization. The frontier orbital approximation is particularly excellent for nucleophilic "one-bond" reagents.

Coulombic effects may also come into play with charged or highly polarized nucleophiles. That is, as the site of attack on the cyanoalkene becomes more strongly positively charged, the attack of negatively charged nucleophiles will be facilitated. However, for reasonable nucleophile-cyanoalkene transition-state separations (2.5-3.5 Å), the total Coulombic interaction changes by only a few kcal/mol, because although the Coulombic attraction for alkene carbons rapidly increases as more cyano groups are attached to the vinyl group, the repulsion between the nucleophile and the cyano nitrogen, the site of largest negative charge in the cyanoalkenes, gives a compensatory increase in repulsion as the number of cyano groups is increased.

Mechanisms of Polar [2 + 2] Cycloadditions

For cycloadditions of cyanoalkenes to nucleophilic alkenes such as enol ethers, there seems to be ample evidence for formation of zwitterionic intermediates, but Epiotis has recently proposed that these reactions can involve concerted mechanisms, if the charge-transfer configuration is lower in

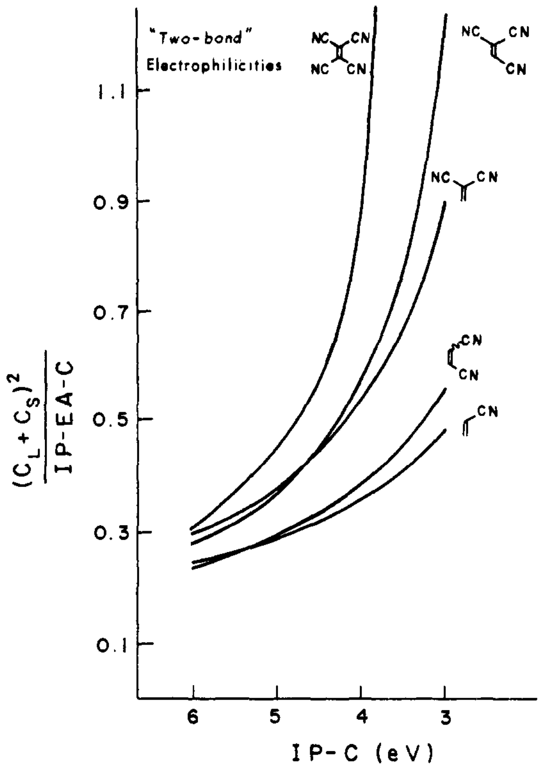

Figure 9. Calculated "two-bond" electrophilicities of cyanoalkenes as a function of the nucleophile IP.

energy than the "ground configuration". If the charge-transfer configuration is lowest in energy, then it can be stabilized by mixing with the excited configurations[3] or, equivalently, by HOMO-HOMO and HOMO-LUMO interactions. Typical shapes for the frontier MO's of unsymmetrical electron-rich and electron-defficient alkenes are shown in Figure 11. For a stepwise mechanism, the reaction of unsymmetrical alkenes will be stabilized by HOMO (donor)-LUMO (acceptor) interactions, and the more stabilized transition state will involve union of the sites of larger coefficients. The experimentally observed "head-to-head" product will be obtained. By contrast, if the charge-transfer configuration is lowest in energy as proposed by Epiotis, the HOMO-HOMO and LUMO-LUMO interactions will be maximized by union of the larger coefficients. The HOMO-HOMO interactions will favor formation of the "head-to-head" isomer, but the LUMO-LUMO interactions will favor "head-to-tail" adduct formation. Little preference for one over another isomer is expected, unless Coulombic effects override the frontier orbital interactions.

Since high "head-to-head" regiospecificity is observed in polar cycloadditions,[40] one-bond mechanisms, rather than concerted two-bond mechanisms involving a lowest energy charge-transfer configuration are implicated. Further confirmatory evidence for the one-bond (or stepwise, zwitterionic) mechanism for reactions of electron-rich alkenes could be obtained by a study of the rates of addition of an electron-rich alkene to the whole series of alkenes. The stepwise mechanism should follow "one-bond" electrophilicities, while rates of reaction by the Epiotis mechanism would follow the EA of the cyanoalkene and the alkene electronic absorption energies.

Reactions of Cyanoalkenes with Radicals and as Excited State Quenchers

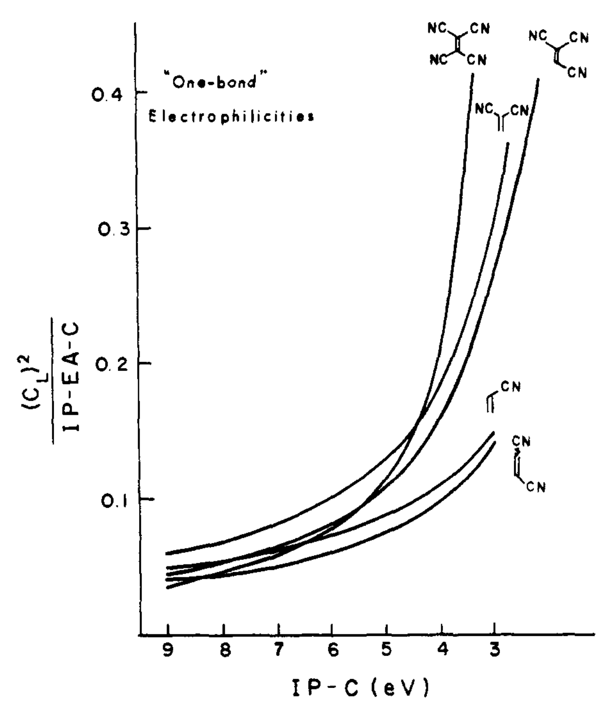

Figure 10. Calculated "one-bond" electrophilicities of cyanoalkenes as a function of the nucleophile IP.

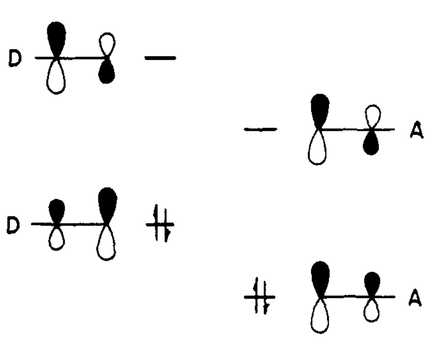

Figure 11. Typical frontier orbitals of an electron-rich and an electron-deficient alkene.

In reactions of alkenes with radicals, interaction of the radical singly occupied orbital (SOMO) with either the alkene HOMO or LUMO, or both, may be important.[1] Since quantitative rate data are not available for additions of a single radical to all the cyanoalkenes, details will not be discussed here, but we will note that the "one-bond" electrophilicities shown in Figure 9 should apply to "electron-rich", or nucleophilic radical additions also. On the other hand, electrophilic radicals will follow more nearly the "one-bond" nucleophilicities shown in Table III, where CNDO/2 calculated coefficients and the IP's reported here are used for the calculations. A model electrophile of EA = 2 eV was chosen for the calculation. Both the "one-bond" and "two-bond" electrophilicities change by relatively small amounts along the series, since the IP's change by relatively small amounts. Since there is a more or less regular decrease in coefficients as the IP increases, few changes in relative reactivity will be observed with a change in electrophile EA. Only vinylidene cyanide deviates from the otherwise regular decrease in reactivity with increasing ionization potential, and this is due to the large terminal coefficient.

Returning to the question of radical reactivity, qualitative data are available, indicating that in styrene copolymerizations, vinylidene cyanide reacts several orders of magnitude faster than acrylonitrile, maleonitrile, or fumaronitrile with the polystyryl radical,[41] in qualitative agreement with the "one-bond" electrophilicities of these compounds.

Table III. "One-Bond" and "Two-Bond" Nucleophilicities of Cyanoalkenes

Compound	C_L	C_S	IP	$\frac{(C_L)^2}{IP - 2 - 4}$	$\frac{(C_L + C_S)^2}{IP - 2 - 4}$
Acrylonitrile	0.60	0.49	10.92	0.073	0.24
Maleonitrile	0.50	0.50	11.15	0.049	0.19
Fumaronitrile	0.50	0.50	11.15	0.049	0.19
Vinylidene cyanide	0.61	0.45	11.38	0.069	0.21
Tricyano-ethylene	0.52	0.47	11.55	0.049	0.18
Tetracyano-ethylene	0.45	0.45	11.79	0.035	0.14

Turro and coworkers have recently studied the rates of fluorescence quenching of ketone excited states by cyanoalkenes,[42] and they suggested that the cyanoalkene LUMO interaction is crucial in determining the quenching rate. The $n\pi^*$ singlets of acetone and adamantanone are quenched 22 and 50 times faster, respectively, by fumaronitrile than by acrylonitrile. This is in accord with the action of the cyanoalkenes as "two-bond" electrophiles, as suggested by Turro. Furthermore, the greater sensitivity of the adamantanone singlet quenching to a change in cyanoalkene is compatible with its expected lower ionization potential.

Conclusion

The measurement or estimation of experimental vertical IP's and EA's of cyanoalkenes, along with calculated coefficients for the frontier orbitals of these species, has made the calculation of reactivity indexes possible. The behavior of cyanoalkenes toward "one-bond" and "two-bond" nucleophiles is quite different, so that a theoretical criterion for concertedness in cycloadditions is established. The cyanoalkenes are particularly amenable to frontier orbital treatments, since steric effects are negligible in these planar molecules. Similar treatments of substituted alkenes involving groups which are both electronically perturbing and sterically demanding are subjects of continuing investigations.

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References and Notes

(1) K. Fukui, *Fortsch. Chem. Forsch.*, **15**, 1 (1970), and references therein.
(2) (a) K. N. Houk, *Acc. Chem. Res.*, **8**, 361 (1975); (b) K. N. Houk in "Pericyclic Reactions", R. E. Lehr and A. P. Marchand, Ed., Academic Press, N.Y., in press.
(3) N. D. Epiotis, *Angew. Chem., Int. Ed. Engl.*, **13**, 751 (1974), and references therein.
(4) R. F. Hudson, *Angew. Chem., Int. Ed. Engl.*, **12**, 36 (1973), and references therein.
(5) R. Sustmann, *Tetrahedron Lett.*, 2717, 2721 (1971); R. Sustmann and H. Trill, *Angew. Chem., Int. Ed. Engl.*, **11**, 383 (1972); R. Sustmann and R. Schubert, *ibid.*, **11**, 840 (1972).
(6) K. N. Houk, *J. Am. Chem. Soc.*, **94**, 8953 (1972); **95**, 4092 (1973); J. Sims and K. N. Houk, *ibid.*, **95**, 5798 (1973); K. N. Houk, J. Sims, R. E. Duke, Jr., R. W. Strozier, and J. K. George, *ibid.*, **95**, 7287 (1973); K. N. Houk, J. Sims, C. R. Watts, and L. J. Luskus, *ibid.*, **95** 7301 (1973); K. N. Houk, J. K. George, and R. E. Duke, Jr., *Tetrahedron*, **30**, 523 (1974).
(7) T. Koopmans, *Physica*, **1**, 104 (1934).
(8) See for example, C. Muller, A. Schweig, and H. Vermeer, *J. Am. Chem. Soc.*, **97**, 982 (1975), and references therein.
(9) R. F. Lake and H. Thompson, *Proc. R. Soc. London, Ser. A*, **317**, 187 (1970).
(10) H. Bock and H. Stafast, *Chem. Ber.*, **105**, 1158 (1972). Since the completion of this manuscript, we have become aware that Bock and Stafast have also carried out photoelectron spectroscopic studies of vinylidene cyanide and tetracyanoethylene: H. Stafast, Dissertation, Frankfurt am Main, 1974. A more complete analysis of the higher ionization potentials may be found in this reference.
(11) D. W. Turner, C. Beker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy", Wiley-Interscience, London, 1970.
(12) D. C. Frost, F. G. Herring, C. A. McDowell, and I. A. Stenhouse, *Chem. Phys. Lett.*, **4**, 533 (1970).
(13) R. Sustmann and H. Trill, *Tetrahedron Lett.*, 4271 (1972).
(14) A. L. Farragher and F. M. Page, *Trans. Faraday Soc.*, **63**, 2369 (1967).
(15) K. Kimura and S. Nagakura, *Theor. Chim. Acta*, **3**, 164 (1965).
(16) V. Kaldor and I. Shavitt, *J. Chem. Phys.*, **48**, 191 (1968).
(17) W. J. Hehre, unpublished results.
(18) G. Briegleb, *Angew. Chem., Int. Ed. Engl.*, **3**, 617 (1964).
(19) I. G. Sevast'yanova and A. P. Tomilov, *Zh. Obshch. Khim.*, **33**, 2815 (1963).
(20) S. K. Smirnov, I. G. Sevast'yanova, A. P. Tomilov, L. A. Fedorova, and O. G. Strukov, *Zh. Obshch. Khim.* **5**, 1392 (1969).
(21) P. H. Rieger, I. Bernal, W. H. Reinmuth and G. K. Fraenkel, *J. Am. Chem. Soc.*, **85**, 683 (1963).
(22) T. L. Cairns and B. C. McKusick, *Angew. Chem.*, **73**, 520 (1961).
(23) B. M. Hughes, C. Lifshitz, and T. O. Tiernan, *J. Chem. Phys.*, **59**, 3162 (1973).
(24) M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **34**, 11 (1938); M. G. Evans and E. Warhurst, *ibid.*, **34**, 614 (1938); M. G. Evans, *ibid.*, **35**, 824 (1939).
(25) A. I. Konovalov, V. D. Kiselev, and O. A. Vigdorovich, *J. Org. Chem. USSR Engl. Transl.*, **3**, 2034 (1967).
(26) K. Best, M. Christl, R. Huisgen, and W. Mack, *Chem. Ber.*, **106**, 3312 (1973).
(27) N. E. Schore and N. J. Turro, *J. Am. Chem. Soc.*, **97**, 2482 (1975), and references therein.
(28) P. S. Skell and M. S. Cholod, *J. Am. Chem. Soc.*, **91**, 7131 (1969).
(29) J. Sauer, H. Wiest, and A. Mielert, *Chem. Ber.*, **97**, 3183 (1964).
(30) The ionization potential of 9,10-dimethylanthracene was estimated as 7.02 eV by assuming that the change in IP from that of anthracene (IP = 7.40 eV)[31] is directly proportional to the square of the coefficient at the site of methyl attachment, using the difference between *p*-xylene (8.6 eV)[32] and benzene (9.25 eV)[11] as standards. The ionization potential, calculated in this way for 9-methylanthracene (7.21 eV), is quite close to a recent experimental determination (7.25 eV).[33]
(31) P. A. Clark, F. Brogli, and E. Heilbronner, *Helv. Chim. Acta*, **55**, 1415 (1972).
(32) M. Klessinger, *Angew. Chem., Ed. Engl.*, **11**, 525 (1972).
(33) S. Hino and H. Inokuchi, *Chem. Lett.*, 363 (1974).
(34) G. Klopman, *J. Am. Chem. Soc.*, **90**, 223 (1968).
(35) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory", McGraw-Hill, New York, N.Y., 1970.
(36) O. Eisenstein and N. T. Anh, *Tetrahedron Lett.*, 1191 (1971).
(37) A. E. Ardis, S. J. Averill, H. Gilbert, F. F. Miller, R. F. Schmidt, F. D. Stewart, and H. L. Trumbull, *J. Am. Chem. Soc.*, **72**, 1305, 3127 (1950).
(38) H. A. Bruson, *Org. React.*, **5**, 79 (1949).
(39) O. W. Webster, W. Mahler, and R. E. Benson, *J. Am. Chem. Soc.*, **84**, 3678 (1962).
(40) R. Gompper, *Angew. Chem., Int. Ed., Engl.*, **8**, 312 (1969).
(41) J. Brandrup and E. H. Immergut, Ed., "Polymer Handbook", Interscience, New York, N.Y., 1966.
(42) N. J. Turro, C. Lee, N. Schore, J. Barltrop, and H. A. J. Carless, *J. Am. Chem. Soc.*, **93**, 3079 (1971).
(43) H. Bock, G. Wagner, K. Wittel, J. Sauer, and D. Seebach, *Chem. Ber.*, **107**, 1869 (1974).
(44) K. Wittel and H. Bock, *Chem. Ber.*, **107**, 317 (1974).