J. Org. Chem. **1992**, *57*, 1139–1145 1139

The reactions with the nitromethide ion were conducted in a Durrum-Gibson stopped-flow apparatus with double mixing capability. In the first mixing process nitromethane was reacted with 0.5 equiv of KOH to produce a 1:1 NM/NM$^-$ buffer. After a few seconds, this latter solution was reacted with the substrate in the second mixing process.

Equilibrium Measurements. The equilibrium constants for piperidine addition (K_{eq}) were measured spectrophotometrically at the wavelengths reported in Table S8.[10] These wavelengths were chosen such that the respective β-nitrostyrene was the only contributor to the absorbance. Due to competing hydrolysis[13] OD readings decreased with time and, in most cases, had to be determined in the stopped-flow apparatus by extrapolation to "zero time" with respect to the hydrolysis reaction. To minimize errors, OD_0 readings were taken from the same substrate solution that was used for the OD measurements in the presence of piperidine.

Acknowledgment. This research was supported by Grant CHE-8921739 from the National Science Foundation.

Supplementary Material Available: Kinetic and equilibrium measurements, Tables S1–S8 (10 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

A Theoretical Analysis of the Relative Reactivity in Radical Addition Reactions: Acceptor–Donor, Acceptor–Acceptor, and Donor–Donor 1,1-Disubstituted Ethenes. The Effect of Ground-State Destabilization on Reactivity

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Ab initio theoretical calculations have been carried out on a number of acceptor–donor, acceptor–acceptor, and donor–donor 1,1-disubstituted ethenes and on related monosubstituted ethenes and 2-substituted propenes. Ground-state effects in the 1,1-disubstituted ethenes have been evaluated using the isodesmic reaction

Acceptor–donor and acceptor–acceptor 1,1-disubstituted ethenes suffer considerable ground-state destabilization, while the donor–donor disubstituted ethenes vary considerably from enjoying a high degree of ground-state stabilization to a high degree of destabilization. The 1,1-disubstituted systems possessing significant ground-state destabilization also possess relatively low-lying LUMOs. The relative reactivity data [ln k_{rel}] for the addition of alkyl free radicals to monosubstituted ethenes and 2-substituted propenes produces a linear correlation with the energy of the LUMO. The limited relative reactivity data for the free-radical addition to the 1,1-disubstituted ethenes also gives a very reasonable linear correlation with the energy of the π LUMOs. The regioselectivity of the alkyl free-radical addition processes is also consistent with a FMO-controlled process, the attack occurring at the 2p AO of the LUMO possessing the largest coefficient which is at C_2 of the acceptor–donor and acceptor–acceptor 1,1-disubstituted ethenes.

Introduction

The effect of substituents on the relative reactivity and regioselectivity in radical addition reactions with substituted alkenes has been an area of intense interest. In general, it has been observed that the presence of an electron-withdrawing group on the alkene increases the reactivity of the substituted alkene toward alkyl radical addition.[1-6] What appears to be the first rationalization of the relative reactivity of substituted alkenes in radical addition reactions was by Fukui and co-workers, who suggested that reactivity is controlled by a dominant radical SOMO–alkene LUMO interaction.[7] This suggestion was later criticized on the basis that the energy gap between the SOMO of the free radical and the HOMO of the alkene must be smaller than that between the SOMO of the free radical and the LUMO of the alkene, leading to the conclusion that the reactivity and regioselectivity of the radical addition reactions must be SOMO–HOMO-controlled.[8] SOMO–HOMO control was claimed to be supported by the results of calculations.[9] In an early review of the kinetics and orientation of free-radical addition to olefins, Tedder and Walton concluded that the rate and orientation of free-radical addition reactions

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depend on a "complex interplay of polar, steric and bond-strength effects".[10] More recently, the effect of a substituent on the reactivity of an alkene toward free-radical addition has been described as being due to a "polar effect" and rationalized in terms of FMO control in a very early transition state involving a dominant radical SOMO–alkene LUMO interaction.[11] Fischer has also suggested that the reactivity of alkyl free-radical addition reactions is SOMO–LUMO-controlled and has observed a very reasonable linear correlation of the log of the rate constants for alkyl free-radical addition to monosubstituted ethenes, 2-propenes, and some 1,1-disubstituted ethenes with the experimental electron affinities of the substituted alkenes.[12]

The regioselectivity of the addition of alkyl radicals to substituted alkenes has been described as being influenced by polar,[11] steric,[10,11] bond-strength,[10] and electronic (phasing of orbital interactions)[8] effects.

The addition of alkyl free radicals to 1,1-disubstituted alkenes has also received considerable attention. 1,1-Captodative (acceptor–donor) substituted alkenes undergo the facile addition of the isobutyronitrile radical at 75–80 °C to produce relatively stable intermediate free radicals which do not undergo polymerization but instead undergo only dimerization or coupling wih the isobutyronitrile radical.[13] The effect of captodative substitution on the relative stability of the newly formed radical center and on the relative energies of the HOMO and the LUMO of the captodatively-substituted alkene has been discussed in general terms.[14] It has been proposed that captodative substitution reduces the HOMO–LUMO energy gap, thus affecting the reactivity of the system.[14]

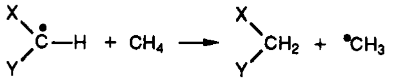
Although much attention has been focused on the reactivity of 1,1-captodative-substituted alkenes, much less attention has been devoted to the factors affecting the relative reactivities of free-radical addition to 1,1-diacceptor- or 1,1-didonor-substituted alkenes. Giese et al. have measured the relative rates of the addition of the cyclohexyl radical to a number of 1,1-disubstituted ethenes.[15] The 1,1-diacceptor-substituted ethenes are, in fact, more reactive than the most reactive of the acceptor–donor-disubstituted ethenes.[15] This has been interpreted in terms of "polar effects" involving a dominant SOMO–LUMO interaction between the radical and the substituted alkene.[11,15] There appears to be no relative reactivity data for alkyl free-radical additions to didonor-substituted alkenes.

Recent theoretical studies in the author's laboratories have focused on the effects of various substituents on the electronic structure and stabilization afforded the radical center.[16,17] In the initial study begun in 1984, the radical stabilization energies (RSEs) of a large number of monosubstituted radicals were calculated according to the isodesmic reaction shown in eq 1 in which the RSE is defined

$$X{-}\dot{C}H_2 + CH_4 \rightarrow X{-}CH_3 + {}^{\bullet}CH_3 \qquad (1)$$

as the difference in the sum of the calculated total energies of the products minus the sum of the total energies of the reactants.[16] These calculations were carried out using the 4-31G basis set and the UHF method for the radical species except when X was a π functional group. When X was a π functional group, for example, in the allyl radical, extensive contributions of higher spin state wave functions to the UHF wave function were indicated by the results of the calculations, and the ROHF method was used resulting in better correlations of calculated results with experimental results. The calculated RSEs indicate the relative ability of a substituent to stabilize, or destabilize, a radical center relative to that of the hydrogen atom whose RSE by definition is 0.00.[16] Excellent correlations of the calculated RSEs with available kinetic and thermodynamic data were obtained.[16]

The effect of two substituents on the stabilization of a radical center was addressed in our second study[17] in an attempt to gain an understanding of the proposed "captodative effect",[18] i.e., that an acceptor–donor substituted radical should enjoy a greater net stabilization than the sum of the stabilizations afforded the singly substituted radical centers.[18] The RSEs of a large number of disubstituted methyl radicals were calculated according to the isodesmic reaction shown in eq 2.[17] Again, the



$$XY\dot{C}{-}H + CH_4 \rightarrow XYCH_2 + {}^{\bullet}CH_3 \qquad (2)$$

4-31G basis set was used as described above in order to utilize the results of the earlier calculations on the monosubstituted methyl radicals and methanes in that study. These RSEs reflect the total stabilization afforded the radical center by the X and Y groups versus two hydrogen atoms, with any geminal interaction between the two substituents in the disubstituted methyl radicals and methanes expected to effectively cancel. ΔRSEs were calculated according to eq 3, the ΔRSEs reflecting any net "extra" stabilization (positive ΔRSE) or destabilization (negative ΔRSE) of the radical center by the X and Y groups.

$$\Delta RSE = RSE_{XY} - (RSE_X + RSE_Y) \qquad (3)$$

Certain combinations of acceptor and donor substituents do produce a net "extra" stabilization, while other conbinations result in a net destabilization.[17] Interestingly, certain diacceptor-substituted radicals were calculated to enjoy a net "extra" stabilization, for example, the dicyanomethyl radical, which is not consistent with the "captodative effect" concept as applied to the stabilization of radical centers. It was concluded that the "captodative effect" concept is not universally valid and that electronegativity effects play an important role in determining the "net" stabilization or destabilization of a radical center.[17] It was also proposed that ground-state effects might be more important than transition-state effects in determining the relative reactivities in certain reactions.[17] The present paper addresses the effects of geminal substitution on the energy of the ground state of a 1,1-disubstituted alkene which will affect the heighth of the energy barrier for the formation of a radical center in the alkyl free-radical addition reactions of various 1,1-disubstituted alkenes.

Results and Discussion

Calculations. Ab initio molecular orbital calculations have been carried out on a number of mono- and disubstituted ethenes and 2-substituted propenes and on the

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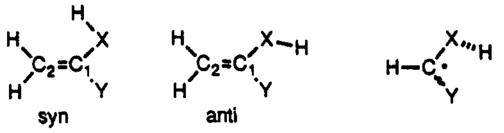
Table I. 4-31G Total Energies (Hartrees) of Substituted Methanes and Methyl Radicals

X	Y	methane	methyl radical
F	Cl	−597.260 37	−596.623 55
F	SH	−535.903 81	−535.267 80
OH	OH	−189.627 91	−189.000 60
OH	NH_2	−169.824 43	−169.201 52
OH	Cl	−573.283 98	−572.653 11
OH	SH	−511.923 55	−511.293 43
NH_2	Cl	−553.494 95	−552.862 52
NH_2	SH	−492.126 22	−491.501 00
BH_2	Cl	−523.754 68	−523.135 64
BH_2	SH	−462.394 35	−461.784 36
Cl	SH	−895.583 73	−894.949 75
Cl	CN	−590.122 02	−589.491 41
Cl	CHO	−611.087 45	−610.460 56
SH	H	−437.183 75	−436.548 78
SH	SH	−834.221 72	−833.595 78
SH	CN	−528.765 88	−528.142 35
SH	CHO	−549.730 27	−549.108 92

corresponding disubstituted methyl radicals and methanes represented in eq 2 not included in our earlier study in order to evaluate ground-state effects in 1,1-disubstituted alkenes.[17] The 4-31G basis set[19] was again selected and used as described above in order to use the results of the earlier calculations on the mono- and disubstituted methyl radicals and methanes. The calculations were carried out using the GAUSSIAN86[20] and -88[21] programs. In these calculations alkoxy and alkylthio groups have been abbreviated as hydroxy and mercapto groups and dialkylamino and dialkylboryl groups have been abbreviated as amino and boryl (H_2B) groups. The minimum energy structures for the hydroxy-, mercapto-, amino-, and boryl-substituted alkenes have the substituents planar and residing coplanar with the ethene framework. For the HO- and HS-substituted ethenes there are two minimum-energy conformations, the syn and the anti conformations shown below.



In the corresponding disubstituted methyl radicals and methanes there are also more than a single minimum-energy conformation for the HO- and HS-substituted systems. Calculations have indicated that the conformations similar to that shown are the lowest in energy. In view of the fact that in the alkoxy- and alkylthio-substituted alkenes the alkyl group would prefer to be in the anti conformation and that in a kinetically controlled process the anti conformation of the substituted ethene would go to the conformation shown for the disubstituted radical, all calculations and correlations are based on the anti conformations of the HO- and HS-substituted ethenes.

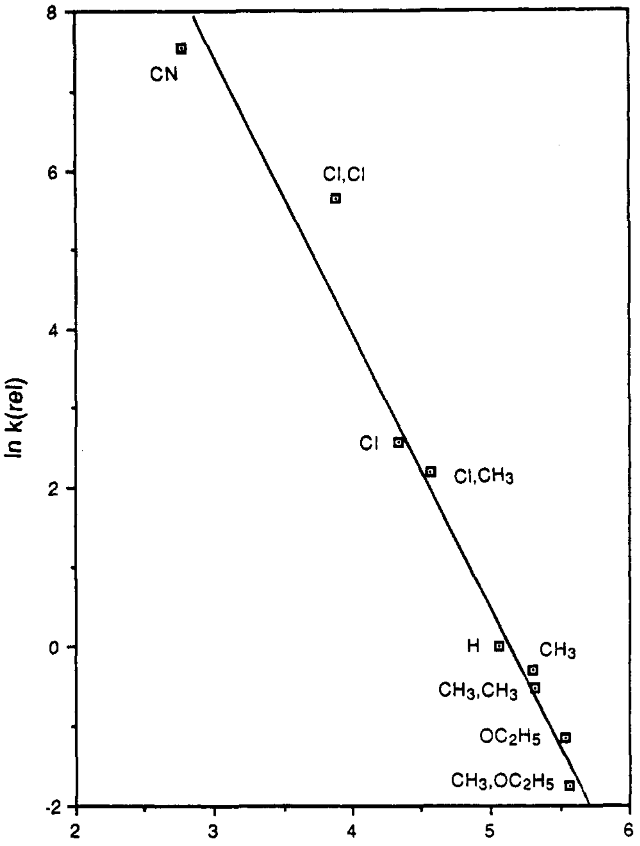
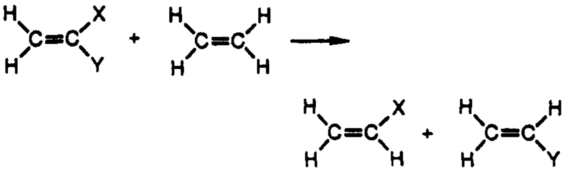


Figure 1. Plot of ln k_{rel} data from ref 12 versus the calculated E_{LUMO}s for mono- and 1,1-disubstituted ethenes and 2-substituted propenes. The calculated correlation coefficient is 0.971.

The total energies of the substituted methyl radicals and methanes are given in Table I, the total energies of the monosubstituted ethenes and propenes are given in Table II, and the total energies of the 1,1-disubstituted ethenes are given in Table III. Also included in Tables II and III are the HOMO and LUMO energies, the HOMO–LUMO energy gaps [$\Delta E_{HOMO-LUMO}$], and the coefficients at C_1 and C_2 of the HOMOs and LUMOs.

ΔE_{tot}s have been calculated for the isodesmic reactions shown in eq 4 and are given in Table IV, along with the


(4)

RSEs for the isodesmic reaction shown in eq 2 and ΔRSEs calculated by using eq 3. Although other isodesmic relationships could have been selected, it is felt that eq 4 would best allow for the evaluation of the effect of the two substituents on the total and π and π* energies of the 1,1-disubstituted ethenes which in turn would have an effect on the relative reactivity toward free-radical addition to the π system.

Correlation of Relative Rates with HOMO and LUMO Energies. Fischer has shown that for a number of mono- and 1,1-disubstituted ethenes (including the 2-substituted propenes in Table II) the log of the relative rates for the addition of the *tert*-butyl radical increase linearly as the electron affinity (EA) of the π system decreases. There is no reasonable correlation between the

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(19) Arguments can be made that a high-level basis set incorporating poplarization function should be used for these calculations. The 4-31G basis set was used in our earlier calculations of the RSEs of mono- and disubstituted methyl radicals (refs 16 and 18), producing excellent correlations with experimental data, and in this study with the ln k_{rel}s for free-radical addition to mono- and 1,1-disubstituted ethenes. To theoretically study such a large number of systems at high-level basis set would not be practical, as is the case also in view of severe convergence problems encountered earlier on calculations of disubstituted methyl and allyl radicals.

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Table II. 4-31G Total Energies (Hartrees) and π HOMO and LUMO Energies (eV) and HOMO and LUMO Coefficients[a] of the Monosubstituted Ethenes and 2-Substituted Propenes

substituent	total energy	E_{HOMO}	E_{LUMO}	$\Delta E_{LUMO-HOMO}$	C_1	C_2
F	−176.651 47	−10.6362	4.8422	15.4784	0.511	0.569
					0.925	0.884
OH(syn)	−152.670 74	−9.5931	5.4803	15.0734	0.440	0.595
					0.970	0.861
OH(anti)	−152.667 31	−9.3925	5.5309	14.9234	0.462	0.575
					0.960	0.877
NH_2	−132.875 21	−8.1153	6.1962	14.3115	0.369	0.592
					1.012	0.848
BH_2	−103.141 97	−10.5372	2.2448	12.7820	0.544	0.511
					0.246	0.607
Cl	−536.327 12	−10.3574	4.3337	14.6911	0.437	0.490
					0.905	0.900
SH(syn)	−474.970 32	−9.0418[b]	4.7867	13.8285	0.318	0.454
					0.930	0.887
SH(anti)	−474.969 11	−8.9811[c]	4.8071	13.7882	0.327	0.448
					0.925	0.900
CN	−169.515 92	−10.7606	2.7686	13.5292	0.490	0.478
					0.628	0.869
CHO(cisoid)	−190.478 14	−10.6531	2.3351	12.9882	0.542	0.487
					0.420	0.686
H	−77.922 16	−10.2047	5.0648	15.2695	0.551	0.551
					0.893	0.893
CH_3	−116.905 10	−9.7011	5.3059	15.0070	0.461	0.560
					0.888	0.869
		2-Substituted Propenes				
CH_3	−155.887 59	−9.3514	5.3195	14.6709	0.573	0.506
					0.821	0.814
OH	−191.653 54	−9.0804	5.5709	14.6513	0.591	0.454
					0.881	0.885
CN	−208.498 47	−10.3734	3.0649	13.4383	0.505	0.496
					0.786	0.647
Cl	−575.313 62	−10.0496	4.5682	14.6178	0.449	0.519
					0.884	0.870

[a] The top row of coefficients is for the HOMO, the bottom row for the LUMO. [b] Dominant contribution from S nonbonded pair AO (c_i ~0.71); π dominant MO at −12.2561 eV. [c] Dominant contribution from S nonbonded pair AO (c_i ~0.71); π dominant MO at −12.2000 eV.

ln k_{rel}s and the presently calculated energies of the π HOMOs. There is, however, a good linear correlation between the ln k_{rel}s and the energies of the π LUMOs as is illustrated in Figure 1.[22] The observation of this linear correlation provides further support for the suggestion that the dominant FMO interaction in the alkyl free-radical addition reactions is between the SOMO of the radical and the LUMO of the substituted alkene.

Analysis of the HOMO and LUMO Energies and $E_{HOMO-LUMO}$s of the 1,1-Disubstituted Ethenes. An analysis of the data given in Table III shows that the range of the energies of the HOMOs of the acceptor–donor (−8.3 to −11.2 eV) and donor–donor (−8.2 to −11.1 eV) disubstituted systems are very similar, while for the acceptor–acceptor disubstituted ethenes (−10.9 to −11.3 eV) the range is much narrower and lower in energy, but yet within the upper range of the other two systems. The ranges of the energies of the LUMOs of the three types of systems, however, are quite different. The energy range for the acceptor–acceptor-disubstituted ethenes (1.2 to 1.8 eV) is quite low and narrow. The range for the acceptor–donor-disubstituted systems (1.6 to 3.4 eV) is considerably broader and higher in energy. The range for the donor–donor-disubstituted ethenes (3.9 to 6.7 eV) is broad and very much higher in energy.

There is no correlation between the energy of the π HOMOs and the ln k_{rel}s for the addition of the cyclohexyl radical to the α-substituted acrylonitriles.[23,24] However, there is a reasonable correlation between the ln k_{rel}s and the energy of the π LUMOs which is shown in Figure 2. (The one point which does not correlate well is that for ethoxyacrylonitrile which has been modeled in the calculations by hydroxyacrylonitrile.) It is important to note that in this correlation there are representatives of acceptor–donor- *and* acceptor–acceptor-1,1-disubstituted ethenes. The linear correlation indicates a dominant SOMO–LUMO interaction in these alkyl free-radical addition processes.

There is no correlation between the $\Delta E_{HOMO-LUMO}$ and the ln k_{rel}s of the α-substituted acrylates and acrylonitriles.

Relationship of ΔE_{tot}s with Type of Substitution. The ΔE_{tot}s, calculated as the change in total energy for the isodesmic reaction shown in eq 4, show very interesting trends. The ΔE_{tot}s reflect the effect of the two substituents on the ground-state energy of the 1,1-disubstituted ethenes relative to that of the monosubstituted ethenes. Of the acceptor–acceptor-disubstituted ethenes, the α-substituted borylethenes show slight ground-state destabilization (−1.46 kcal mol^{-1}) to slight stabilization (1.95). All of the substituted acrylonitriles have substantially negative values of ΔE_{tot}s (−3.39 to −6.39), indicating the presence of substantial ground-state destabilization. The substituted

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[22] The linear correlations between the ln k_{rel}s and EAs and between the ln k_{rel}s and the calculated energies of the π LUMOs implies a linear correlation between the EAs and the energies of the π LUMOs which indicates that the use of the 4-31G basis set without the inclusion of polarization functions was a valid and reasonable approach.

[23] Data from ref 11.

[24] An attempt was made to correlate the calculated quantities of the α-substituted acroleins with the relative rate data for the addition of the cyclohexyl radical to the α-substituted acrylates (refs 11 and 15) on the assumption that the relative HOMO and LUMO energies of the substituted acroleins and acrylates would parallel each other. However, no reasonable correlation was obtained. Calculations on the α-substituted acrylates were not carried out because of the additional number of AOs in the basis set and the larger number of possible conformations for the substituted ethenes, methyl radicals, and methanes.

Table III. 4-31G Total, π HOMO, and LUMO Energies, $\Delta E_{\mathrm{HOMO\text{-}LUMO}}$, and Coefficients[a] of the π HOMOs and LUMOs of 1,1-Disubstituted Ethenes

X	Y	total energy (hartrees)	E_{HOMO} (eV)	E_{LUMO} (eV)	$\Delta E_{\mathrm{HOMO\text{-}LUMO}}$	C_1	C_2
			Donor–Acceptor Systems				
F	BH_2	−201.873 54	−10.8025	1.6402	12.4427	0.503 0.233	0.530 0.570
OH	BH_2	−177.888 50	−9.7661	2.1039	13.3254	0.430 0.232	0.553 0.536
NH_2	BH_2	−158.092 70	−8.2892	2.3686	10.6578	0.349 0.183	0.549 0.508
Cl	BH_2	−561.550 03	−10.4556	1.5795	12.0351	0.407 0.265	0.438 0.606
SH	BH_2	−500.191 03	−9.0728	1.9379	11.0107	0.288 0.257	0.407 0.586
F	CN	−268.235 04	−11.2275	2.3672	13.5947	0.478 0.604	0.511 0.760
OH	CN	−244.256 19	−10.3772	2.9482	13.3254	0.439 0.636	0.553 0.737
NH_2	CN	−224.436 57	−9.0636	3.4205	12.4841	0.380 0.621	0.563 0.706
Cl	CN	−627.910 79	−10.9305	2.2157	13.1462	0.439 0.634	0.469 0.798
SH	CN	−556.557 20	−9.7364	2.5838	12.3202	0.338 0.633	0.432 0.784
F	CHO	−289.206 48	−11.0605	1.8187	12.8792	0.512 0.396	0.518 0.636
OH	CHO	−265.226 67	−10.0956	2.3691	12.4647	0.460 0.408	0.551 0.606
NH_2	CHO	−245.427 15	−8.7052	2.6573	11.3625	0.394 0.365	0.551 0.566
Cl	CHO	−648.880 61	−10.7652	1.7654	12.5306	0.458 0.430	0.459 0.679
SH	CHO	−587.523 32	−9.5163	2.1267	11.6430	0.339 0.430	0.426 0.661
			Acceptor–Acceptor Systems				
BH_2	BH_2	−128.357 70	−10.8545	1.7545	12.6090	0.541 0.228	0.474 0.695
CN	BH_2	−194.735 83	−10.8953	1.2832	12.1785	0.476 0.289	0.438 0.674
CHO	BH_2	−215.698 61	−10.9108	1.3964	12.3072	0.535 0.260	0.446 0.694
CN	CN	−261.096 21	−11.3143	1.3156	12.9299	0.481 0.565	0.444 0.806
CHO	CN	−282.067 21	−11.1413	1.2065	12.3478	0.506 0.438	0.438 0.739
CHO	CHO	−303.031 47	−11.0422	1.1684	12.2106	0.542 0.349	0.434 0.728
			Donor–Donor Systems				
F	F	−275.381 31	−11.1114	4.7573	15.8687	0.595 0.864	0.484 0.952
OH_a	F	−251.402 10	−10.1070	5.4357	15.5427	0.427 0.996	0.620 0.843
NH_2	F	−231.611 16	−8.7811	6.1252	14.9063	0.364 1.035	0.615 0.836
Cl	F	−635.046 25	−10.8028	4.2942	15.0970	0.535 0.885	0.443 0.938
SH	F	−573.691 49	−9.6581	4.7105	14.3686	0.327 0.958	0.487 0.876
OH_a	OH_a	−227.421 17	−9.3286	6.0223	15.3509	0.384 1.041	0.649 0.819
NH_2	OH	−207.631 11	−8.1928	6.6928	14.8856	0.340 1.081	0.649 0.812
Cl	OH	−611.067 96	−9.9870	4.9141	14.9011	0.576 0.800	0.414 0.909
SH	OH	−549.713 22	−9.0973	5.2825	14.3798	0.325 1.005	0.540 0.854
Cl	NH_2	−591.278 85	−8.8211	5.5554	14.3765	0.590 0.857	0.372 1.023
SH	NH_2	−529.920 55	−8.2445	5.9225	14.1670	0.346 1.046	0.602 0.843
Cl	Cl	−994.719 49	−10.5546	3.8861	14.4407	0.499 0.903	0.428 0.922
SH	Cl	−933.368 04	−9.4981	4.2937	13.7918	0.340 0.939	0.465 0.896
SH	SH	−872.012 31	−9.0031	4.6153	13.6184	0.324 0.985	0.506 0.878

[a] The top row of coefficients are for C_1 and C_2 (see structure in text) of the HOMO, the lower row for the LUMO.

Table IV. RSEs, ΔRSEs, ΔE_{tot}s, and (RSE – ΔE_{tot})s for the 1,1-Disubstituted Ethenes[a,b]

X	Y	RSE	ΔRSE	ΔE_{tot}	RSE – ΔE_{tot}
		Acceptor–Donor Systems			
F	BH_2	16.41	2.87	1.42	14.99
OH_a	BH_2	22.41	4.88	–1.29	23.70
NH_2	BH_2	26.63	4.64	–1.46	28.09
Cl	BH_2	11.88	1.37	1.95	9.93
SH	BH_2	18.16	4.56	0.56	17.60
F	CN	5.95	–1.22	–6.39	12.34
OH_a	CN	12.14	–0.86	–5.21	17.35
NH_2	CN	16.73	4.64	–3.39	20.12
Cl	CN	4.62	–0.23	–6.33	10.95
SH_a	CN	7.55	3.77	–3.87	11.42
F	CHO	8.82	–0.67	–0.61	9.43
OH_a	CHO	17.90	4.42	–1.56	19.16
NH_2	CHO	22.47	4.53	–2.53	25.00
Cl	CHO	6.96	–0.21	–1.63	8.59
SH	CHO	10.43	0.88	–1.93	12.36
		Acceptor–Acceptor Systems			
BH_2	BH_2	13.74	–9.68	–2.56	16.30
CN	BH_2	14.96	–2.19	0.06	14.90
CN	CN	11.17	0.49	–8.45	19.62
CHO	CN	12.35	–0.65	–2.94	15.29
CHO	CHO	14.73	–0.59	–1.66	16.39
		Donor–Donor Systems			
F	F	1.22	–2.44	0.33	0.89
OH_a	F	–0.81	–8.46	1.29	–2.10
NH_2	F	5.33	–6.78	4.17	1.16
Cl	F	0.73	–0.42	–6.39	7.12
SH	F	1.23	–2.49	–5.11	6.34
OH_a	OH_a	6.69	–4.77	6.85	–0.16
NH_2	OH_a	9.46	–6.33	0.43	9.03
Cl	OH_a	4.46	–0.78	–0.77	5.23
SH	OH_a	4.93	–3.19	–3.56	8.49
Cl	NH_2	2.85	–6.92	–0.81	3.66
SH	NH_2	8.01	–4.16	–1.77	9.78
Cl	Cl	0.30	1.28	–7.90	8.20
SH_a	Cl	2.51	0.61	–3.78	6.29
SH_a	SH_a	7.55	3.77	–3.87	11.42

[a] All values are in kcal mol^{-1}. [b] Subscript a's indicate an anti conformation.

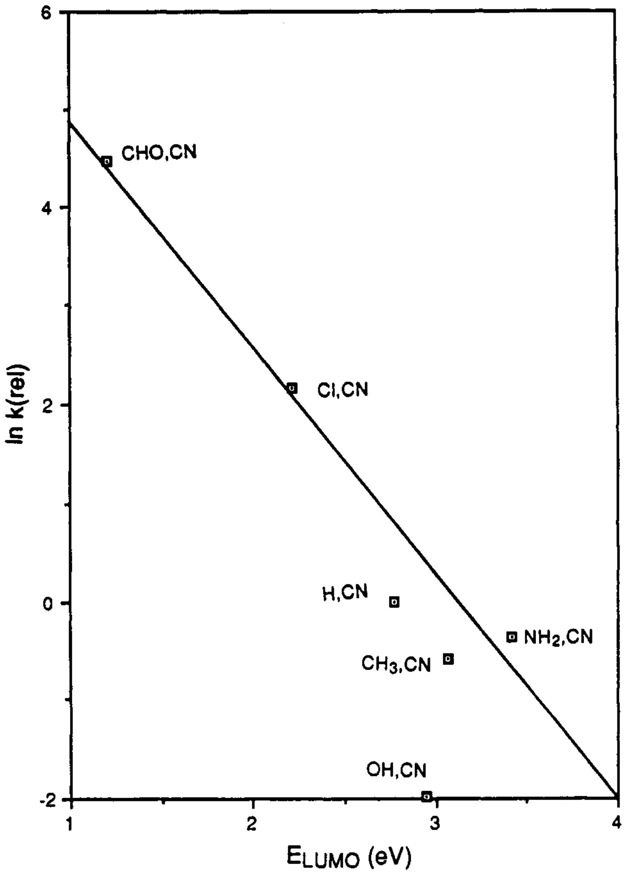

Figure 2. Plot of ln k_{rel} data from ref 11 versus the calculated E_{LUMO}s for α-substituted acrylonitriles. The calculated correlation coefficient is 0.829 for all points.

acroleins all show slight to moderate (–0.61 to –2.53) ground-state destabilization.

The ΔE_{tot}s for the few acceptor–acceptor-substituted systems studied vary considerably. It must be noted, however, that 1,1-dicyanoethene suffers the largest ground-state destabilization (–8.45 kcal mol^{-1}) of any system included in this study. 1,1-Dicyanoethene is well known to be extremely reactive toward free-radical addition, which must be due, in part or wholly, to this ground-state destabilization. α-Cyanoacrolein also suffers significant ground-state destabilization (–2.94), which must contribute to its high reactivity toward alkyl free-radical addition.[11,15]

The ΔE_{tot}s of the donor–donor-disubstituted ethenes cover a considerable range of values, from highly ground-state-stabilizing [NH_2–F (+4.17); OH–OH (+6.85)] to highly ground-state-destabilizing [Cl–F (–6.39); SH–F (–5.11); Cl–Cl (–7.90)]. It is simply interesting to note at this time that 1,1-dichloro- and 1-chloro-1-fluoro-substituted alkenes are quite reactive toward free-radical addition,[12] while 1,1-dialkoxy-substituted alkenes appear to be quite unreactive toward free-radical addition.

Comparison of the RSEs and ΔRSEs of the 1,1-Disubstituted Ethenes. The RSEs of the acceptor–donor-substituted methyl radicals are, in general, substantial in magnitude, indicating a high degree of stabilization of the radical center. As we have noted previously, the magnitude of the ΔRSE (eq 3) depends strongly on the relative electronegativities of the acceptor and donor groups,[17] being highly stabilizing in the H_2N–H_2B disubstituted systems and significantly destabilizing in the HO–CN and F–CN disubstituted systems. The RSEs of the acceptor–acceptor-disubstituted radicals indicate significant stabilization of the radical center, but the negative values of the ΔRSEs indicate net destabilization relative to the sum of the stabilizations afforded the monosubstituted radicals, *except* with the CN–CN system. The RSEs of the donor–donor-disubstituted systems are all substantially smaller than those of the two other systems, and the vast majority of the ΔRSEs indicate a net destabilization of the disubstituted systems relative to the sum of the stabilizations afforded the monosubstituted systems.

There is no correlation of the RSEs with ln k_{rel}. The transition states for the addition of alkyl free radicals to substituted alkenes appear to occur very early along the reaction coordinate before substantial radical character is developed at C_1.

Other Possible Reactivity Correlations. From the results of prior investigations and the results described above, the relative reactivities of the 1,1-disubstituted alkenes toward alkyl free-radical addition appears to be FMO SOMO–LUMO-controlled, with the high degree of reactivity of the acceptor–acceptor- and acceptor–donor-disubstituted alkenes arising from ground-state destabilization of the π system by the attached substituents. There appears to be no direct correlation of relative reactivity toward alkyl free-radical addition with the stability of the radical being formed as judged by the lack of any apparent correlation of ln k_{rel} with the RSE values.

The possibility of ground-state effects and radical product stability both contributing to the reactivity of the substituted alkenes toward free-radical addition has also been evaluated. Such a correlation might involve the value of (RSE − ΔE_{tot}), the ground-state destabilization (stabilization) effectively lowering (raising) the energy barrier for free-radical addition, with increasing values of RSE acting to lower the energy barrier. The values of (RSE − ΔE_{tot}) are given in Table IV. It must be noted that, except for a few cases, the values of (RSE − ΔE_{tot}) for the acceptor–donor-disubstituted ethenes are substantial in magnitude, which should result in the lowering of the energy barrier for the free-radical addition process. The same is true for the acceptor–acceptor-disubstituted systems. The values of (RSE − ΔE_{tot}) for the donor–donor-disubstituted ethenes, however, are in general rather small in magnitude, thus having a lesser inpact on the heighth of the energy barrier for free-radical addition. In general, high reactivity toward free-radical addition is associated with large positive values of (RSE − ΔE_{tot}). The plot of ln k_{rel} versus (RSE − ΔE_{tot}), however, does not show a good correlation between the two quantities. Because of the lack of a sufficient amount of relative reactivity data for free-radical addition to 1,1-disubstituted alkenes, no attempt has been made to correlate the relative reactivity data with variations in the relative extents of the contributions of the two quantities.

Regioselectivity of Free-Radical Addition to Mono- and 1,1-Disubstituted Ethenes. The regioselectivity of free-radical addition to mono- and 1,1-disubstituted ethenes has been interpreted in terms of polar,[11] steric,[10,11] and bond-strength[10] effects. The present results suggest that the relative reactivity in alkyl free-radical addition reactions to substituted alkenes occurs very early along the reaction coordinate, which is free-radical SOMO–alkene LUMO-controlled. One might ask if the regioselectivity of the addition process is also FMO-controlled, i.e., by the relative magnitudes of the coefficients on C_1 and C_2 in the LUMO of the alkene.

In the monosubstituted ethenes the largest coefficient in the LUMO appears at C_1 except with the π-accepting H_2B-, NC-, and CHO-substituted systems in which the largest coefficient appears at C_2. However, in many of the cases the coefficients are quite similar in magnitude and steric effects, which would affect the distance between the attacked carbon atom and the free radical and thus the overlap intergral between the interacting orbitals, could easily reverse the regioselectivity from that based solely on the relative magnitudes of the coefficients. Acrylonitrile and acroylein are known to undergo attack only at C_2. In all of the acceptor–donor-disubstituted ethenes the largest coefficient in the LUMO resides at C_2, the position of exclusive free-radical attack. In all of the acceptor–acceptor-disubstituted ethenes the largest coefficient in the LUMO also resides at C_2, again the position of exclusive free-radical addition. In the donor–donor-disubstituted ethenes there appears to be no apparent trend, the largest coefficient appearing in some at C_1 and in others at C_2. It should be noted that the coefficients are much greater in magnitude than those in the other two systems and are also very similar in magnitude. In this case there is very little experimental information for which to make a comparison with.

Summary

The ln k_{rel}s for the addition of alkyl free-radical to 1,1-disubstituted ethenes correlates linearly with the energy of the LUMO of the substituted ethenes. The most reactive of the 1,1-disubstituted ethenes suffer the greatest amount of ground-state destabilization as measured by their values of ΔE_{tot}. These 1,1-disubstituted ethenes contain highly electronegative substituents (CN–CN; F–CN; HO–CN; Cl–CN; CN–CO_2R) and fall into both acceptor–donor and acceptor–acceptor classes of functionalized ethenes. The presence of the two highly electronegative groups results in a substantial lowering of the energy of the LUMO of the π system, thus resulting in high reactivity toward free-radical addition. The values of (RSE − ΔE_{tot}), which reflect ground-state destabilization and product radical stabilization, do not correlate with the ln k_{rel}s for free-radical addition. This is undoubtedly due to the fact that the transition state for free-radical addition occurs so early along the reaction coordinate such that very little radical character is developed in the transition states for radical addition.

The regioselectivity of the alkyl free-radical addition to the acceptor–donor- and acceptor–acceptor-1,1-disubstituted ethenes appears to be controlled by the relative magnitudes of the 2p AO coefficients in the LUMO of the substituted alkenes, being larger at C_2 than at C_1, and not by the stability of the incipient radical center.

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