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Substituent Effects on Ketene Structure and Stability: An ab Initio Study[1a]

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Abstract: Calculated structures and energies of ketenes RCH=C=O (R = H, Li, BeH, BH_2, CH_3, NH_2, OH, F, Na, MgH, AlH_2, SiH_3, PH_2, SH, Cl, c-Pr, CH=CH_2, C≡CH, CF_3, CH=O, CN, NC, N=O, CO_2H, CH=C=O) at the 6-31G*/6-31G* level reveal major stabilization by electropositive groups and destabilization by electronegative substituents. There is a good correlation of substituent stabilization of ketenes defined by ΔE for the isodesmic reaction RCH=C=O + CH_3CH=CH_2 → CH_3CH=C=O + RCH=CH_2 and group electronegativities χ_{BE} reported by Boyd and Edgecombe. Thus the primary stabilizing influence of substituents on ketenes is evidently by σ-electron donation to the electronegative ketene moiety. There is also evidence that substituents stabilize ketenes by π withdrawal and destabilize ketenes by n–π donation. The calculated substituent effects on ketenes are compared to known experimental results and to the corresponding effects on allenes and on β-ethyl carbocations.

Because of the fascinating electronic structure of ketenes these species have frequently been the subject of investigation by molecular orbital (MO) methods.[1-4] These studies have focussed on the electronic structure of ketene itself,[2] the reaction of ketenes with protons[1c,3] and nucleophiles,[1b] cycloaddition of ketenes with alkenes[4a,b,e,f] and dialkoxyalkynes,[4i] and rearrangements of conjugated ketenes.[4g,h]

Many substituted ketenes have been generated and their properties observed,[5a-h] and while it is clear that bulky groups decrease ketene reactivities there has been no consistent interpretation proposed of how the electronic properties of substituents affect ketene reactivities. The current investigation uses ab initio molecular orbital calculations to make a broad survey of the effect of representative substituents on the ground states of ketenes and uses this information to understand ketene structures and reactivities. This study is also relevant to current studies of substituent effects on allenes,[5i,j] alkenes,[5k-m] carbanions,[5n] carbocations,[5o] and other species.[5p] As described below this study reveals a quantitative dependence of the stabilizing effect of ketene substituents on their group electronegativities, such that the most electropositive substituents are the most stabilizing. There is also evidence that π acceptor substituents stabilize and π donor substituents destabilize ketenes, and together with group electronegativities these provide a consistent basis for interpreting the stabilizing effects of the many types of ketene substituents that have been studied.

Methodology and Results

Standard ab initio molecular orbital calculations were carried out with use of the MONSTERGAUSS program and the GAUSSIAN 88 package[6a] on Apollo DN10000 and SUN 3-260 minicomputers. Geometry optimization was achieved by gradient techniques with the Optimally Conditioned method.[6b] All stationary points were optimized at the Hartree–Fock (HF) level by using the split-valence 6-31G* basis set.[6b] All critical points were determined at 3-21G by numerically differentiating the analytical first derivatives of the restricted Hartree–Fock wave function.

The structures and energies of a variety of substituted ketenes and the corresponding alkenes were calculated at several levels of theory. Values of the ketene energies as well as ΔE values for the isodesmic reaction of eq 1 at the 3-21G//3-21G and 6-31G*//6-31G* levels are presented in Table I. Literature data[5i] for the comparable reaction of allenes (eq 2) calculated at the 6-31G//6-31G level are also given in Table I. It was found in

$$\mathrm{RCH{=}C{=}O + CH_3CH{=}CH_2 \rightarrow CH_3CH{=}C{=}O + RCH{=}CH_2} \quad (1)$$

$$\mathrm{RCH{=}C{=}CH_2 + CH_3CH{=}CH_2 \rightarrow CH_3CH{=}C{=}CH_2 + RCH{=}CH_2} \quad (2)$$

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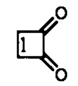
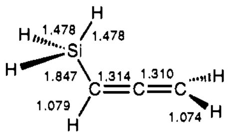
Table I. Energies (hartrees) for Ketenes RCH=C=O and Alkenes $RCH=CH_2$ and ΔE (kcal/mol) for the Isodesmic Reaction of Equation 1

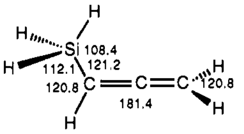
	$-E$(RCH=C=O)		$-E$($RCH=CH_2$)		ΔE		ΔE_{allene}[a]	
R	3-21G//3-21G	6-31G*//6-31G*	3-21G//3-21G	6-31G*//6-31G*	3-21G//3-21G	6-31G*//6-31G*	6-31G//6-31G	χ_{BE}[b]
H	150.8765	151.7247	77.6010	78.0317	2.9	3.3	1.2	2.20
Li	157.7009	158.5935	84.3866	84.8614	27.2	27.9	14.0	1.00
BeH	165.4440	166.3753	92.1451	92.6587	17.6	18.1		1.47
BH_2	176.0115	177.0041	102.7146	103.2897	16.3	16.8		1.93
CH_3	189.6949	190.7592	116.4240	117.0715	0.0	0.0	0.0	2.56
NH_2	205.5827	206.7382	132.3264	133.0620	−9.2	−7.2	−5.1	3.10
OH	225.2888	226.5540	152.0418	152.8889	−15.0	−14.2	(−4.4)[c]	3.64
F	249.1625	250.5422	175.9206	176.8820	−18.2	−17.2	−5.4	4.00
Na	311.1509	312.9798	237.8338	239.2456	29.0	29.2		1.00
MgH	349.3475	351.3195	276.0428	277.5969	21.2	21.9		1.33
AlH_2	392.0582	394.2252	318.7574	320.5076	18.8	18.7		1.62
SiH_3	439.5385[d]	441.8176	366.2509[d]	368.1125	10.5[d]	10.9	4.1[e]	1.91
PH_2	490.5506[d]	493.0237	417.2693[d]	419.3259	6.5[d]	6.3		2.17
SH	546.5408	549.2317	473.2676	475.5419	1.5	1.3		2.63
Cl	607.6828[d]	610.6094	534.4236[d]	536.9337	−7.3[d]	−7.5		3.05
CF_3	484.6847	487.3439	411.4155	413.6568	−1.1	−0.4		2.68
c-Pr	266.1237	267.6250	192.8559	193.9402	−1.9	−1.8		2.56
$CH=CH_2$	227.3300[f]	228.6070	154.0595	154.9197	−0.2	−0.2	0.0	2.61
CH=O	262.9659	264.4559	189.6899	190.7624	3.3	3.6	1.2	2.60
CO_2H	337.4469	339.3488	264.1677	265.6536	5.2	4.7	−0.3	2.66
C≡CH	226.1270	227.3959	152.8562	153.7079	−0.1	0.2	−1.2	2.66
CN	242.0901	243.4551	168.8204	169.7680	−0.8	−0.4	−1.0	2.69
CH=C=O[g]	300.5901	302.2832						
CH=C=O[h]	300.5921	302.2858	227.3300	228.6070	−5.3[i]	−5.3[i]		
	300.5855	302.2968						
N=O	278.7688	280.3647	205.5002	206.6774	−1.4	−0.3		3.06
N≡C[j]	242.0476	243.4125	168.7922	169.7384	−9.7	−8.5		3.30

[a] Reference 5h. [b] Group electronegativity from ref 9b, except Pauling electronegativity (ref 9a) for H. [c] OCH_3. [d] 3-21G*//3-21G*. [e] This work, based on E = −405.9466 and −115.8611 hartrees for $SiH_3CH=C=CH_2$ and $CH_2=C=CH_2$, respectively (6-31G*//6-31G*). [f] Reference 1c. [g] Cisoid. [h] Transoid. [i] For the process $(CH=C=O)_2 + (CH_2=CH)_2 \rightarrow 2CH_2=CHCH=C=O$. [j] Isocyano.

this allene study[5i] that there was a negligible difference in ΔE for eq 2 for comparing 6-31G//6-31G with 6-311G**//6-31G level calculations. The calculated bond angles and distances for the ketenes and corresponding substituted ethylenes are given in Tables II and III. The geometrical parameters are also given on structural formulas in somewhat greater detail in Tables VII and VIII (supplementary material). Z matrices are also given in the supplementary material. Since $SiH_3CH=C=CH_2$ was not included in the previous allene study[5i] it was also studied and the calculated energy is included in Table I, and the calculated bond distances (Å) and bond angles (deg) are given on **1a** and **1b**, respectively.



1a



1b

Atomic charges derived from a Mulliken population analysis[6b] for the ketenes and alkenes are given in Tables IV and V, together with calculated dipole moments. We believe the trends reported in Tables IV and V are meaningful, but note that there are several alternative methods for the calculation of atomic charges[6c–f] and that this topic is controversial.[6g] The method of Bader et al.,[6c,d] for calculation of charges using gradient vector fields, or the natural population analysis of Weinhold et al.[6e] may give better results.

Discussion

The results in Table I show very little effect of improving the basis set on the quantitative values of ΔE, and so lend assurance that the results are not highly basis set dependent and that even higher level calculations would not affect the conclusions drastically. Values of ΔH_f° are available for the ketenes $CH_2=C=O$,[7a] $CH_3CH=C=O$,[7b] and $CH_2=CHCH=C=O$[7c] of −14.6, −20.6, and 4 kcal/mol, respectively, and together with ΔH_f° = 12.4 and 4.7 kcal/mol for ethylene and propylene, respectively,[7d] these lead to $\Delta\Delta H^\circ_f$ values for the reaction of eq 1 of 1.8 and −3.1 kcal/mol for the H and $CH_2=CH$ groups, respectively. These are in reasonable agreement with the calculated values of 3.3 and −0.2 kcal/mol, respectively, and thus the calculated values are probably within the experimental uncertainties of the measured values.

Experimental geometries derived from microwave spectra are available for ketenes substituted with H,[8a] CH_3,[8b] F,[8c] and Cl[8d] and are compared in Table VI to the calculated structures. Of 16 independent bond length comparisons the calculated values are shorter in 15, and the average difference is 0.011 Å.

In a previous theoretical and experimental study of fluoroketene it was noted that there were systematic deviations between the experimental and theoretical geometries, and empirical corrections to theoretical geometries were suggested.[8e] The use of MP2/4-31G** calculations for fluoroketene gave "uncorrected" lengths of the CO, CC, CH, and CF bonds of 1.181, 1.323, 1.074, and 1.363 Å, respectively.[8e] These latter calculated values are longer in three of four cases than the experimental values (Table VI), and the average difference between the calculated and experi-

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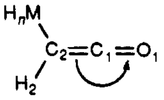
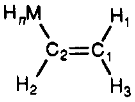
Table II. Bond Distances (Å) and Bond Angles (deg) Calculated (6-31G*//6-31G*) for Ketenes



M	$C_1{=}O_1$	$C_1{=}C_2$	$C_2{-}H_2$	$C_2{-}M$	$M{-}H$	$O_1C_1C_2$	C_1C_2M	MC_2H_2	HMC_2
H	1.145	1.306	1.071			180.0	119.3	121.4	
Li	1.163	1.290	1.077	1.946		184.8	118.3	124.1	
BeH	1.144	1.309	1.079	1.659	1.332	182.1	122.1	123.2	179.4
BH_2	1.134	1.327	1.075	1.519	1.190	181.3	117.7	126.3	120.1
CH_3	1.149	1.305	1.074	1.512	1.084	180.0	123.3	120.8	110.9, 111.4
NH_2	1.145	1.313	1.076	1.423	1.000	178.9	118.6	124.4	111.9
OH	1.147	1.312	1.072	1.374	0.948	178.7	120.4	120.5	109.3[a]
F	1.147	1.308	1.067	1.339		177.9	120.1	117.4	
Na	1.171	1.282	1.074	2.273		185.6	113.8	125.7	
MgH	1.152	1.299	1.078	2.058	1.711	183.4	122.4	122.3	177.8
AlH_2	1.142	1.312	1.078	1.922	1.580	182.2	121.6	123.2	118.9, 118.3
SiH_3	1.143	1.308	1.077	1.860	1.475	181.1	122.0	122.5	108.3, 110.9
PH_2	1.142	1.309	1.073	1.825	1.402	181.3	123.4	119.6	100.8
SH	1.140	1.313	1.072	1.766	1.329	180.0	119.7	122.0	99.4[b]
Cl	1.142	1.308	1.068	1.731		179.2	120.8	118.7	
CF_3	1.137	1.312	1.071	1.484	1.324[c]	178.8	120.9	120.2	110.9[d]
c-Pr	1.149	1.305	1.074	1.494	1.076	179.8	123.3	120.8	120.3
$CH{=}CH_2$	1.144	1.312	1.074	1.467	1.077[e]	179.8	122.6	121.3	116.2[f]
$CH{=}O$	1.136	1.321	1.073	1.463	1.094[g]	180.4	120.7	121.2	115.6
CO_2H	1.134	1.322	1.071	1.458	1.335[h]	178.6	121.3	120.2	124.8[i]
$C{\equiv}CH$	1.139	1.317	1.073	1.428	1.188[j]	179.0	121.3	121.8	179.1[k]
CN	1.133	1.321	1.072	1.424	1.137[l]	178.7	120.6	121.3	179.4[k]
$C{=}C{=}O$[m]	1.148	1.307	1.073	1.476		180.7	123.2	121.1	
$C{=}C{=}O$[n]	1.147	1.308	1.073	1.479		179.2	127.0	117.9	
	1.175	1.502[o]	1.071	1.337[p]		136.9[q]	137.3[r]	132.4[s]	
$N{=}O$	1.131	1.330	1.072	1.400	1.185[t]	179.1	115.9	123.2	114.4[u]
$N{\equiv}C$	1.139	1.317	1.070	1.376	1.157[v]	178.1	121.0	119.9	177.7[w]

[a] HOC_2C_1 (84.2°). [b] HSC_2C_1 (97.3°). [c] CF (av). [d] FCC (av). [e] $CH_2{=}CH$ (1.322 Å). [f] CH_2CHC (124.5°). [g] $CH{=}O$ (1.190 Å). [h] $C{-}O$, $C{=}O$ (1.188 Å), $O{-}H$ (0.952 Å). [i] $O{-}CC$, HOC (108.2°). [j] $C{\equiv}C$, $C{\equiv}C{-}H$ (1.057 Å). [k] $C{\equiv}C{-}C$. [l] CN. [m] Transoid. [n] Cisoid. [o] $C{-}C$. [p] $C{=}C$. [q] $O{=}C{-}C$. [r] $O{=}C{-}CO$. [s] $C{-}C{-}H$, $H{-}C{=}C$ (133.4°). [t] $N{=}O$. [u] $O{=}N{-}C$. [v] $N{-}C$. [w] CNC.

Table III. Bond Distances (Å) and Bond Angles (deg) Calculated (6-31G*//6-31G*) for Alkenes



M	$C_1{-}C_2$	$C_1{-}H_1$	$C_1{-}H_3$	$C_2{-}H_2$	$C_2{-}M$	$M{-}H$	$H_1C_1H_3$	$H_3C_1C_2$	C_1C_2M	MC_2H_2	HMC_2
H	1.317	1.076					116.4	121.8	121.8	116.4	
Li	1.337	1.084	1.085	1.089	1.975		113.2	124.3	119.2	128.4	
BeH	1.332	1.079	1.079	1.083	1.684	1.336	114.5	123.1	121.8	122.8[a]	181.1
BH_2	1.331	1.076	1.078	1.080	1.551	1.192	115.8	122.8	121.1	121.1	119.4, 121.8
CH_3	1.318	1.077	1.076	1.079	1.502	1.087	116.5	121.7	125.2	115.9	111.4, 110.9
NH_2	1.322	1.077	1.073	1.077	1.393	0.998	117.3	120.6	126.7	113.3	114.2
OH	1.318	1.077	1.073	1.074	1.347	0.948	117.6	120.1	126.9	110.7	110.4
F	1.309	1.074	1.073	1.072	1.329		118.7	119.8	122.4	111.9	
Na	1.335	1.084	1.086	1.090	2.300		113.1	124.2	120.5	127.2	
MgH	1.333	1.081	1.082	1.084	2.090	1.719	113.8	123.3	121.6	124.0	181.3
AlH_2	1.332	1.078	1.079	1.082	1.950	1.586	115.0	122.9	121.0	122.6	121.3, 118.0
SiH_3	1.325	1.077	1.078	1.080	1.874	1.478	115.6	122.2	123.6	118.7	110.9, 109.1
PH_2	1.320	1.076	1.076	1.079	1.832	1.403	116.2	121.4	126.2	114.9	98.5
SH	1.317	1.076	1.075	1.076	1.768	1.326	116.9	120.3	127.8	111.5	98.1
Cl	1.311	1.074	1.075	1.071	1.737		118.0	119.6	123.3	112.9	
CF_3	1.314	1.075	1.074	1.074	1.494	1.324[a]	117.1	120.9	123.5	114.1	112.0[a]
c-Pr	1.320	1.077	1.075	1.080	1.483	1.077[g]	116.6	121.6	125.1	115.8	114.6
$CH{=}CH_2$	1.323	1.077	1.075	1.078	1.468	1.078	116.6	121.7	124.1	116.3	116.3
$CH{=}O$[b]	1.321	1.077	1.075	1.075	1.478	1.095	116.4	121.1	121.3	116.3	115.3
CO_2H	1.320	1.074	1.075	1.074	1.481	1.331[c]	117.2	121.0	123.9	113.9[d]	
$C{\equiv}CH$	1.322	1.075	1.075	1.076	1.439	1.188[e]	117.3	120.9	123.8	115.9	
CN	1.320	1.074	1.074	1.074	1.443	1.136[f]	117.3	120.7	122.2	115.8	
NO	1.318	1.074	1.074	1.076	1.424	1.182[g]	117.9	121.7	117.8	116.6	113.7[h]
NC	1.316	1.074	1.073	1.073	1.385	1.156[i]	118.1	120.1	123.0	114.1	177.7[j]

[a] $C{-}F$ (av). [b] OMC_2 (123.8°), $CH{=}O$ (1.190 Å). [c] $C{-}OH$, $C{=}O$ (1.189 Å), $O{-}H$ (0.952 Å). [d] $C{-}O{-}H$, $O{=}C{-}O$ (123.3°), $O{=}C{-}C$ (123.6°). [e] $C{\equiv}C$, $C{\equiv}C{-}H$ (1.057 Å). [f] $C{\equiv}N$. [g] $N{=}O$. [h] $O{=}NC$. [i] NC. [j] CNC.

mental bond lengths only decreases from 0.021 to 0.016 Å, compared to our 6-31G* results. Bond distances for fluoroallene calculated with the 6-31G* basis set are also consistently less than the measured values, by an average of 0.014 Å.[5i]

For both 6-31G* and MP2/4-31G[8e] basis sets the calculated bond angles are close to the experimental values, and the latter

Table IV. Net Atomic Charges[a] on Ketenes $H_nMC_2H_2{=}C_1{=}O_1$ (6-31G*//6-31G*)

M	O_1	C_1	C_2	M	H_2	H_n	μ, D
H	-0.44	0.57	-0.61	0.24	0.24		1.63
Li	-0.55	0.54	-0.69	0.51	0.18		7.39
Be	-0.45	0.53	-0.55	0.30	0.24	-0.07	1.47
B	-0.41	0.58	-0.52	0.19	0.24	-0.04	1.08
C	-0.45	0.53	-0.37	-0.48	0.23	0.18	1.99
N	-0.44	0.58	-0.23	-0.83	0.21	0.36	2.90
O	-0.43	0.53	-0.07	-0.70	0.22	0.46	2.33
F	-0.41	0.48	0.06	-0.36	0.23		1.59
Na	-0.58	0.49	-0.72	0.61	0.18		9.01
Mg	-0.49	0.56	-0.71	0.53	0.23	-0.12	2.03
Al	-0.44	0.60	-0.72	0.64	0.25	-0.17	1.36
Si	-0.43	0.57	-0.67	0.71	0.25	-0.14	1.39
P	-0.43	0.60	-0.66	0.27	0.26	-0.02	0.44
S	-0.42	0.61	-0.59	0.03	0.26	0.10	1.57
Cl	-0.41	0.60	-0.49	0.02	0.27		1.39
CF_3	-0.39	0.59	-0.55	1.16		-0.36[b]	1.88
c-Pr[c]	-0.45	0.50	-0.34	-0.16	0.23	0.20	2.04
$CH{=}CH_2$[d]	-0.43	0.52	-0.37	-0.10	0.24	0.20	1.20
CH=O	-0.39	0.57	-0.46	0.35	0.27	-0.16[e]	2.41
CO_2H	-0.39	0.61	-0.51	0.83[f]	0.28		1.12
C≡CH	-0.41	0.58	-0.42	0.14[f]	0.27		1.01
CN	-0.38	0.61	-0.40	0.32	0.30		3.72
CH=C=O	-0.43	0.51	-0.33	-0.33	0.25		0.0
N=O	-0.49	0.62	-0.14	0.03	0.33		2.73
NC	-0.39	0.57	-0.13	-0.40	0.28	0.08[g]	2.73

[a] From Mulliken population analysis. [b] F. [c] C_4 (-0.36), H_4 (0.19). [d] C_4 (-0.42), (*Z*)-H_4 (0.18), (*E*)-H_4 (0.17). [e] O_3 (-0.51). [f] C_4 (-0.46), H_4 (0.29). [g] C_4.

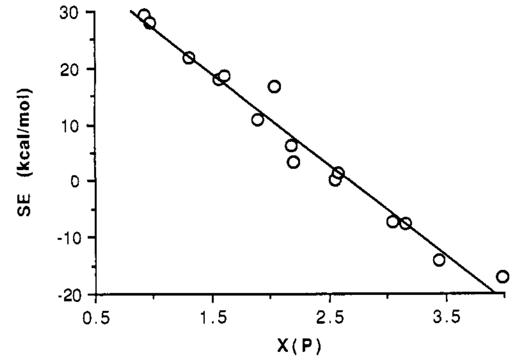


Figure 1. Isodesmic stabilization energy (SE, kcal/mol) of ketenes by substituents versus Pauling electronegativities.

basis set data are closer by less than 0.1° on average for fluoroketene. Of all the comparisons in Table VI only for the vinyl H in methylketene is there a major difference between the calculated and experimental bond angles, and the experimental value[8b] is so different from all the other calculated and experimental values that we believe the calculated value to be more reliable.

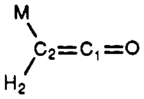
We conclude that calculations at a higher level than 6-31G* would give geometries that are only marginally closer to experimental geometries, and that the measurement of bond lengths for other ketenes by microwave spectroscopy may be anticipated to give modestly longer values on average than the calculated values reported here. Unpublished experimental results on cyanoketene[8h] give comparable agreement with our calculated values

Table V. Net Calculated Atomic Charges on Alkenes $H_nMC_2H_2{=}C_1H_1H_3$ (6-31G*//6-31G*)

M	C_1	C_2	M	H_1	H_2	H_3	H_n	μ, D
H	-0.35	-0.35	0.18	0.18	0.18	0.18	0.18	0.0
Li	-0.36	-0.39	0.43	0.12	0.10	0.12		5.95
Be	-0.37	-0.29	0.24	0.16	0.17	0.17	-0.08	0.69
B	-0.33	-0.31	0.20	0.19	0.18	0.18	-0.06	1.17
C	-0.40	-0.12	-0.51	0.17	0.17	0.18	0.17	0.31
N	-0.47	0.10	-0.86	0.16	0.19	0.36	0.36	1.54
O	-0.50	0.21	-0.71	0.16	0.20	0.18	0.45	1.06
F	-0.47	0.26	-0.37	0.20	0.19			1.53
Na	-0.40	-0.41	0.50	0.10	0.09	0.12		7.27
Mg	-0.36	-0.40	0.44	0.14	0.15	0.16	-0.13	0.48
Al	-0.33	-0.44	0.60	0.18	0.18	0.18	-0.18	0.86
Si	-0.35	-0.42	0.66	0.18	0.19		-0.15	0.80
P	-0.36	-0.37	0.23	0.18	0.20		-0.03	1.13
S	-0.38	-0.30	0.00	0.18	0.22	0.19	0.09	1.26
Cl	-0.35	-0.25	-0.04	0.21	0.23	0.20		1.85
CF_3	-0.36	-0.30	1.11	0.23	0.22	0.20	-0.37[a]	2.50
c-Pr	-0.42	-0.09	-0.21	0.17	0.18	0.17	0.19	0.45
$CH{=}CH_2$	-0.41	-0.14	-0.41	0.18	0.19	0.18	0.18	0.0
CH=O	-0.37	-0.23	0.32	0.20	0.22	0.20	0.15[b]	3.51
CO_2H	-0.35	-0.26	0.76	0.21	0.23			2.38
C≡CH	-0.36	-0.17	0.11	0.20	0.22	0.19	-0.47[c]	0.47
CN	-0.34	-0.17	0.28	0.21	0.24		-0.45[f]	4.26
N=O	-0.39	-0.05	0.00	0.26	0.27	0.25	-0.34[d]	3.42
NC	-0.39	0.08	-0.42	0.21	0.23	0.20	-0.42[e]	3.20

[a] F. [b] O (-0.49). [c] C_4 (-0.47), H_4 (0.29). [d] O_4. [e] C_4 (0.08). [f] N.

Table VI. Calculated 6-31G* and Experimental (Parentheses)[8] Bond Distances (Å) and Bond Angles (deg) of Ketenes



	C=O	$C_1{=}C_2$	$C_2{-}H_2$	$C_2{-}M$	M—H	OC_1C_2	C_1C_2M	MC_2H_2	$C_1C_2H_2$	HMC_2
H	1.145	1.306	1.071	1.071		180.0	119.3	121.4	119.3	
	(1.161)	(1.314)	(1.075)	(1.075)		(180.0)	(119.1)	(121.8)	(119.1)	
CH_3	1.149	1.305	1.074	1.512	1.084	180.0	123.2	120.8	116.0	111.4
	(1.171)	(1.306)	(1.083)	(1.518)	(1.085)	(180.5)	(122.6)	(123.7)	(113.7)	(111.4)
F	1.147	1.308	1.067	1.339		177.9	120.1	117.4	122.5	
	(1.167)	(1.317)	(1.102)	(1.360)		(178.0)	(119.5)	(118.2)	(122.3)	
Cl	1.142	1.308	1.068	1.731		179.2	120.8	118.7	120.5	
	(1.161)	(1.316)	(1.082)	(1.726)		(180.0)	(119.8)	(119.3)	(120.9)	

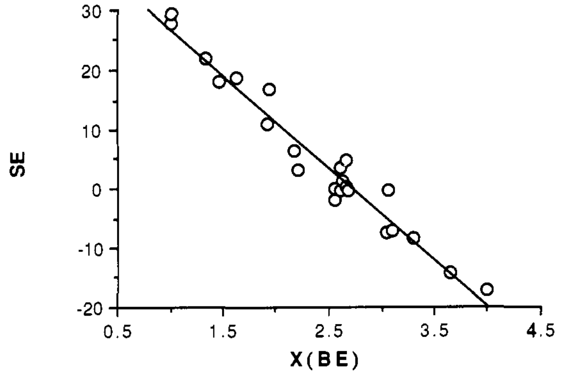


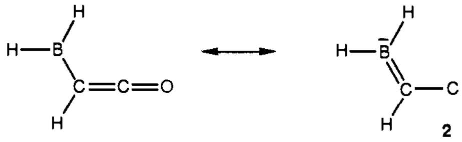
Figure 2. Isodesmic stabilization energy (SE, kcal/mol) of ketenes by substituents versus Boyd–Edgecombe group electronegativities.

shown in Table VI. Both the calculated ketene geometries and the stabilization energies derived from eq 1 are close to experimental values and can be used for a meaningful discussion of substituent effects in ketenes.

Electronegativity Effects. The ΔE values for eq 1 (Table I) show very large effects of substituents on ketene stability, ranging from −17.2 kcal/mol for F to 29.2 kcal/mol for Na. The regular change in ΔE values across the periodic chart suggests a causal relationship, and indeed there is a rather good correlation of ΔE with the Pauling electronegativity values[9a] χ_p for the elements by the relation $\Delta E = -16.2\chi_p + 43.3$, $r = 0.984$ (Figure 1). There has been recent spirited discussion about the definition of electronegativity,[9a-d] and there are several different electronegativity scales. However six different scales which have been compiled[9a] are closely related numerically, and of these the Pauling scale and one derived by Boyd and Edgecombe[9b] give the best correlations of the ketene substituent effects, with $r = 0.984$ for each for the same group of substituents.

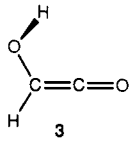
The χ_{BE} values[9b] have the further advantage that they are available for most of the substituents studied here, including HC≡C, CN, etc., but not hydrogen itself, for which the Pauling value of 2.20 is used. These values of χ_{BE} are included in Table I and give the correlation $\Delta E = -15.6\chi_{BE} + 42.3$, $r = 0.978$ (Figure 2). The simplicity and quality of this correlation provides a convincing framework for the interpretation of substituent effects on ketenes based on the stabilization resulting from electron release from the substituent to the ketene moiety.

The stabilization of 12.5 kcal/mol for BH_2 predicted by the correlation of Figure 1 is 4.3 kcal/mol less than that obtained by eq 1 and the extra stabilization for this substituent may be plausibly attributed to π donation from the ketene π system to BH_2, as shown in **2**. The coplanarity of the BH_2, BeH, AlH_2, and MgH substituents with the ketene moiety also suggests that π donation to these groups may be significant. The strongest π acceptor of this group is BH_2 and only for this case are the energetic effects apparent, as the predicted and observed ΔE values are within 1.5 kcal/mol for the other three groups. Similar π acceptor effects were noted for BH_2 and BeH in $RCH{=}CH_2$,[5k] and for ketenes the effect is enhanced by π donation from the carbonyl, as shown.



2

The n–π donor substituents OH and NH_2 however prefer perpendicular conformations **3** and **4**, showing that n–π donation is disfavored for ketenes. In $RCH{=}CH_2$ the OH group is coplanar with the alkene,[11a,b] while NH_2 is close to planar but slightly pyramidalized,[11c] indicating that π donation is stabilizing. However the ketene carbonyl is not conjugated with π donor substituents and so does not enjoy stabilization from such groups.



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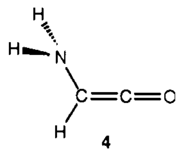

4

Atomic charges calculated from a Mulliken population analysis and calculated molecular dipole moments are also included in Tables IV and V. There have been major reservations expressed about the validity of such calculated atomic charges,[6b] and these should be interpreted with caution. The greatest changes in the atomic charges for ketenes are for C_2, the substituent-bearing carbon, and these charges are approximately correlated with the group electronegativities χ_{BE} of the substituents (charge = $0.24\chi_{BE} - 1.04$, $r = 0.88$).

Experimental and calculated (parentheses) values of dipole moments (D) for ketenes $RCH{=}C{=}O$ are 1.4[8f] (1.63), 1.79[8b] (1.99), 1.29[8c] (1.59), 1.2[8d] (1.39), 0.97[8g] (1.20), and 3.52[8h] (3.72) for R = H, CH_3, F, Cl, $CH_2{=}CH$, and CN, respectively. Thus the theoretical dipole moments are consistently 0.2 D higher than the experimental values, so the calculated dipole moments are useful for predicting the results of experiments.

Comparison to Alkenes and Allenes. Calculations (HF/6-31G*//3-21G) on alkenes $RCH{=}CH_2$ (R = H, F, OH, NH_2, CH_3, BH_2, BeH) led to the conclusion that π donor, π acceptor, and σ acceptor groups were all stabilizing.[5k] We find as noted above that ketenes are stabilized relative to alkenes by electropositive substituents and there is a good linear correlation of this stabilization.

There is a modest correlation between the substituent stabilizations of ketenes and allenes given in Table I, $\Delta E(\text{ketene}) = 2.3\Delta E(\text{allene}) + 0.4$, $r = 0.96$. Previously[5i] correlations were proposed for the allene stabilization energies with the σ_I (inductive) and σ_R (resonance) parameters.[9f-h] However, separate correlations were needed for π donor and π acceptor substituents, and these equations predict ΔE values of 2.8 and 0.7 kcal/mol for the $SiMe_3$ group, respectively. We calculate 4.1 kcal/mol for SiH_3, which fits neither correlation, although the latter correlation would be more appropriate for this group, whose σ_I and σ_R values of −0.10 and 0.06 indicate it to be a σ donor and π acceptor. We conclude that correlation of the ketene stabilizations with the electronegativity parameter χ_{BE}[9b] is much better than the use of σ parameters.

Thus the correlation of ketene stabilization with group electronegativity provides a strong basis for understanding substituent effects on ketene stabilities. These are individual deviations from this correlation, and as discussed above some of these effects may be due to stabilization by π acceptor and destabilization by π donor substituents. Some other specific effects of substituents are discussed below.

Second Period Elements. Fluorine is the most electronegative element, and is also the most destabilizing of the ketene substituents. As discussed above the structure of fluoroketene as

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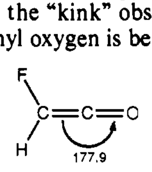
(9) (a) Allen, L. C. *J. Am. Chem. Soc.* **1989**, *111*, 9003–9014. (b) Boyd, R. J.; Edgecombe, K. E. *J. Am. Chem. Soc.* **1988**, *110*, 4182–4186. (c) Boyd, R. J.; Boyd, S. L. In preparation. (d) Pearson, R. G. *Acc. Chem. Res.* **1990**, *23*, 1–2. (e) Allen, L. C. *Acc. Chem. Res.* **1990**, *23*, 175–176. (f) Ehrenson, S.; Brownlee, R. T. C.; Taft, R. W. *Prog. Phys. Org. Chem.* **1973**, *10*, 1–80. (g) Charton, M. *Prog. Phys. Org. Chem.* **1981**, *13*, 119–251. (h) Taft, R. W.; Topsom, R. D. *Prog. Phys. Org. Chem.* **1987**, *16*, 1–83.

(10) (a) Smart, B. E. Fluorocarbons. In *The Chemistry of Functional Groups*, Suppl. D; Patai, S., Rappoport, Z., Eds.; Wiley: London, 1983; Chapter 14, pp 603–655. (b) Smart, B. E. In *Molecular Structure and Energetics*; Liebman, J. F., Greenberg, A., Eds.; VCH, Inc.: Deerfield, FL, 1986; Vol. 3, Chapter 4. (c) Dixon, D. A.; Fukunaga, T.; Smart, B. E. *J. Am. Chem. Soc.* **1986**, *108*, 1585–1588. (d) Reynolds, W. F.; Dais, P.; MacIntyre, D. W.; Topsom, R. D.; Marriott, S.; v. Nagy-Felsobuki, E.; Taft, R. W. *J. Am. Chem. Soc.* **1983**, *105*, 378–384. (e) Brady, W. T.; Hoff, E. F., Jr. *J. Am. Chem. Soc.* **1968**, *90*, 6256. (f) Jacobson, B. M.; Bartlett, P. D. *J. Org. Chem.* **1973**, *38*, 1030–1041. (g) Brady, W. T.; Owens, R. A. *Tetrahedron Lett.* **1976**, 1553–1556.

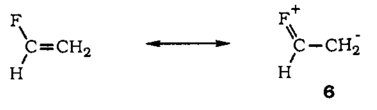
(11) (a) Smith, B. J.; Radom, L. *J. Am. Chem. Soc.* **1990**, *112*, 7525–7528. (b) Apeloig, Y.; Arad, D.; Rappoport, Z. *J. Am. Chem. Soc.* **1990**, *112*, 9131–9140. (c) Saebo, S.; Radom, L. *J. Mol. Struct.* **1982**, *89*, 227–233.

determined by microwave spectroscopy[8c] is close to that calculated here. It is notable that the "kink" observed[8c] in the CCO bond (**5**) such that the carbonyl oxygen is bent away from the fluorine is also seen in the calculated structure (Table II). Similarly in fluoroallene the CCC bond angle is bent by 1.8 ± 0.6° away from the fluorine.[5j] In the ketene this bending is attributed[8c] to electrostatic repulsion between the fluorine and the carbonyl π bond.



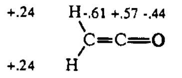
5

The effect of fluorine as a substituent on ethylene has been the subject of much study and discussion,[5k,10b–d] but it is still not resolved. However there is some evidence[10b] that π donation by F as depicted in **6** is important for this structure.



6

The Mulliken population charge distributions calculated for ketenes and alkenes are given in Tables IV and V and are compared for ketene and fluoroketene in **7** and **8**. As noted above these charge distributions are not quantitatively reliable, but the high negative charge of −0.61 calculated for C_2 of ketene is consistent with the remarkably high field ^{13}C NMR chemical shifts of δ 2.5 for this carbon.[5g] Fluorine, because of its high electronegativity, eliminates the adjacent negative charge and creates a dipole opposed to the carbonyl dipole, but it is not known how fluorine effects the ^{13}C chemical shift. Because of the short C–F bond length there is also repulsion between the *n* electron pairs on fluorine and the electron rich π orbital on C_2.[10a,b] The π donor effect of fluorine[10d] is also destabilizing, and the net result is major destabilization by fluorine.



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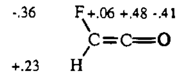
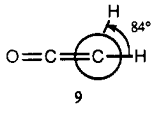


8

Fluoroketene has been generated as a reactive intermediate that was trapped in cycloaddition reactions.[10e,f] The low stability of this species suggests it will be difficult to observe directly in solution. One of the few haloketenes that have been observed in the condensed phase is $Me_3SiCBr{=}C{=}O$, which bears a stabilizing Me_3Si group.[10g]

The OH and NH_2 groups resemble fluorine in being strongly destabilizing as ketene substituents, and the major reason for this can be assigned also to their high electronegativity and to n–π repulsion involving the lone pairs. The OH group adopts the conformation shown in **9** with the O–H bond almost perpendicular to the ketene plane, thus minimizing the interaction of the lone pairs with the alkene π system. A conformation similar to **9** for $HOCH{=}C{=}O$ was also found by MNDO calculations.[4i] The conformation of the NH_2 group is shown (**4**), and the nitrogen lone pair lies in the ketene plane to minimize the π repulsion. Ordinary enols by contrast exist exclusively in the coplanar conformation **10** with the *syn*-OH group.[11a,b] Vinylamine is also calculated to have a conformation in which the NH_2 group is almost coplanar to the double bond and somewhat pyramidalized, thus permitting π donation from the substituent.[11c]



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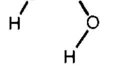
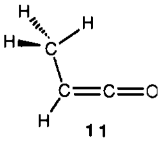


10

The ketene $HOCH{=}C{=}O$ was proposed to form as an unobserved reactive intermediate from photolysis of $CH_2{=}O$ in an Ar matrix,[12a] and $PhC(OH){=}C{=}O$ was formed as a short-lived but observable intermediate during flash photolysis.[12b] There are no reports of $H_2NCH{=}C{=}O$, but substituted aminoketenes are highly reactive but important intermediates in synthesis.[12c–g] Alkoxy- and phenoxyketenes are also useful reactive intermediates,[12h] but earlier reports[12i] of isolation of aryloxyketenes as neat liquids probably dealt with dimeric products.

Nitrosoketene $O{=}NCH{=}C{=}O$ adopts a coplanar conformation in which the N=O group can act as a π acceptor, while the nitrogen lone pair lies in the plane. This is further evidence for the destabilization of ketenes by n–π donation.

Methyl is the prototype of the various carbon substituents on ketene and is calculated to be destabilizing compared to H by the isodesmic reaction of eq 1. This is consistent with the greater electronegativity of C relative to H by the Pauling scale,[9a] and also with the π donor character of methyl.[10d] There is some evidence for methyl acting as a π acceptor,[10d,13] but this effect is minor. The preferred conformation shown in **11** has a substituent hydrogen syn to the ketene group, as is also found for cyclopropyl- and vinylketenes.



11

Cyclopropylketenes have recently been isolated as relatively long lived species at room temperature[1a,14a] and have been known[5e,14b–d] as reactive intermediates. Cyclopropyl is calculated to be destabilizing by 1.8 kcal/mol by eq 1. The stabilizing effect of cyclopropyl on alkenes is well-known,[14e] but this is a π donor effect, which is destabilizing for ketenes, as is the σ acceptor character[14e] of cyclopropyl. The relative kinetic stability of cyclopropylketenes has been attributed to steric effects and a lack of transition-state stabilization.[14a]

Alkenylketenes[15] and alkynylketenes[1a,5f,16] are known as highly reactive intermediates, and the calculations show both groups to be essentially equally stabilizing, consistent with the similar group electronegativities of $CH_2{=}CH$, $HC{\equiv}C$, and CH_3. The former groups function equally well as π donors or acceptors,[10d] and the net effect is no preference relative to CH_3. The high reactivity of the ketenes may be attributed to steric effects, namely the low

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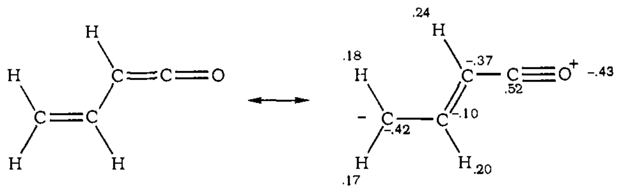
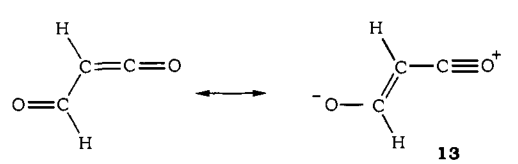
steric requirements of these substituents and their ability to stabilize reaction transition states by conjugation.

The low experimental dipole moment of vinylketene of 0.97 D has been attributed to π electron donation from the ketene moiety as illustrated in resonance structure **12**,[8g] and our calculated dipole moment of 1.20 D is in reasonable agreement with the measured value. Stabilization of the ketene by this interaction is not however established by the energy calculations. The similar calculated atomic charges on oxygen in $CH_2{=}CHCH{=}C{=}O$ (−0.43) and $CH_3CH{=}C{=}O$ (−0.45) and on the terminal carbon in **12** (−0.42) and in 1,3-butadiene (−0.41) also argue against the importance of resonance contributor **12**.



12

Acylketenes are predicted by the calculations to be stabilized, and indeed these species are well-known,[17a-h] display considerably kinetic stability,[18] and have been isolated in some cases.[17f-h] Resonance structure **13** shows the ketene acts as a π donor to the formyl group. Structures **12** and **13** may be compared to dipolar resonance structures frequently drawn for acrolein ($CH_2{=}CH{-}CH{=}O$), but it has recently been suggested[17i] that the latter are of little importance in the ground state. It has however been proposed[17j] that such dipolar structures are more important in polar solvents. The coplanar form of acrolein is significantly stabilized[17i] and the isodesmic reaction of eq 3 has $\Delta E = -3.9$ kcal/mol,



13

$$CH_2{=}CHCH{=}O + CH_2{=}CHCH{=}C{=}O \rightarrow CH_2{=}CHCH{=}CH_2 + O{=}CHCH{=}C{=}O \quad (3)$$

confirming the stabilizing effect in the acylketene. The group electronegativities of $CH{=}O$ (2.60) and CO_2H (2.66) are similar to that of CH_3 (2.56), yet the stabilization energies of the former are 3.6 and 4.7 kcal/mol greater. This greater stability of the carbonyl-substituted ketenes is good evidence for π acceptor stabilization by the substituents.[17k]

Cyanoketones are well-known experimentally but are qualitatively much more reactive than the corresponding acylketenes.[18] The energy calculations indicate that cyano is 4 kcal/mol less stabilizing to the ketene than is CHO, and the lower steric requirement of cyano also would reduce its kinetic stability. The group electronegativities of CN (2.69) and $CH{=}O$ (2.60) are about the same, and the lower stabilizing effect of the former may be ascribed to its poorer π acceptor ability,[10d] and possibly to a destabilizing repulsion of the in-plane sp orbitals of the ketene and cyano groups.

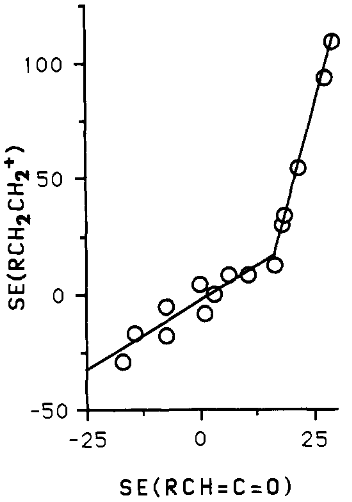
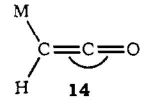


Figure 3. Stabilization energy (SE) of carbocations $RCH_2CH_2^+$ versus stabilization energy (SE) of ketenes $RCH{=}C{=}O$.

All of the ketene substituents more electropositive than methyl are calculated to be stabilizing, and for Li, BeH, and BH_2 these stabilizations are remarkably large, namely 27.9, 18.1, and 16.8 kcal/mol, respectively. The values for the corresponding third row groups (Na, MgH, and AlH_2) are 29.2, 21.9, and 18.7 kcal/mol, respectively. The fact that the stabilization by the third row groups are only modestly larger than the corresponding second row groups, by rather similar amounts of 1.3, 3.8, and 1.9 kcal/mol, respectively, is explained by the electronegativity correlation.

The Li, BeH, and BH_2 substituted ketenes show large MC_2H_2 and C_2C_1O angles of 124.1, 123.2, and 126.3°, and 184.8, 182.1, and 181.3°, respectively, showing the oxygen is bent toward the metal, and the same effect is noted with Na, MgH, and AlH_2. Evidently electrostatic attraction between the oxygen and these electropositive elements causes this effect.



14

There are examples known of ketenes substituted by boron,[19a,b,c] namely $R_3SiC(BR^1_2){=}C{=}O$ ($R^1 = Me_2N$, Br), but as discussed below the silicon substituents are also strongly stabilizing and their influence cannot be readily disentangled from the effect of the boron. With the metalloketenes the question also arises as to whether isomeric structures with C–metal or O–metal bonds (i.e. $RCM{=}C{=}O$ or $RC{\equiv}COM$) are more stable, or whether the species would be ionized, particularly in solution. For lithium these species are known and are formulated as metal ynolates $RC{\equiv}COLi$ or ions in solution.[19d-g] Our calculations at the 3-21G//3-21G level show $HC{\equiv}COLi$ to be more stable than $LiCH{=}C{=}O$ by 18.6 kcal/mol, but at the 6-31G*//6-31G* and MP4/6-31G**//6-31G* levels $LiCH{=}C{=}O$ is more stable by 1.1 and 4.4 kcal/mol, respectively.

Third Period Elements. Comparing the pairs Cl/F, SH/OH, PH_2/NH_2, and SiH_3/CH_3 the third period element substituted ketenes are calculated to be 9.7, 15.5, 13.5, and 10.9 kcal/mol more stable than their second period counterparts (Table I), a result accounted for by the correlation with electronegativity (Figure 1). Chloroketene is calculated to be destabilized by 7.5 kcal/mol by the isodesmic reaction of eq 1, and in practice

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chloroketenes have been widely studied[5c,20] and are indeed quite reactive.

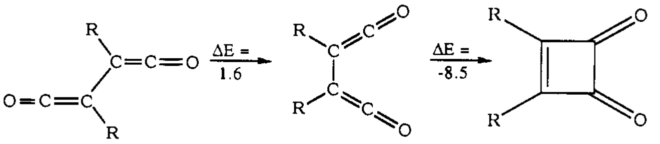
The ketene HSCH=C=O is calculated to be stabilized by 1.3 kcal/mol according to eq 1, and there are many ketenes known with substituents containing α-sulfur atoms, including a variety of $RSCR^1$=C=O (R, R^1 = H, alkyl, aryl),[21a-d] $(RS)_2C$=C=O (R = alkyl, CF_3),[21e-h] ketenes with SO_2R or fluorinated substituents,[22i-p] and $Ph_3SiC(SEt)$=C=O.[21q] Ketenes $RSCR^1$=C=O (R^1 = H, alkyl, aryl) have apparently not been directly observed, but $(RS)_2C$=C=O[21g] and other sulfur-substituted ketenes are isolable as rather long lived compounds.[21h-q]

The PH_2 group is also calculated to be stabilizing by 6.3 kcal/mol by eq 1, and a variety of ketenes are known with phosphoryl substituents ($R_2P(O)CR^1$=C=O: R = alkyl, alkoxy; R^1 = H, alkyl, aryl, acyl).[22a-d] Ylide structures R_3P=C=C=O are also known.[22e,f]

Silylketenes are well-known to be remarkably stable,[23a-h] and this effect is dramatically confirmed by the calculations. This stabilization is expected from the electropositive character of silicon and is also related to the well-known ability of silicon to stabilize an adjacent negative charge.[5n,23j] The ketene $Ph_3SiC(OEt)$=C=O is however quite reactive.[21q] In this case the destabilizing effect of the ethoxy group counterbalances the stabilization due to silicon.

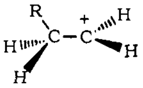
It has been postulated that the stability of silylketenes is due to either σ–π donation from the C–Si bond to the ketene moiety[23c,d] or donation to the d orbitals of silicon.[23g] The former explanation entails a resonance structure $SiH_3^+CH{\equiv}C{-}O^-$, but the respective C=C and C=O bonds in SiH_3CH=C=O and CH_3CH=C=O are calculated to be of almost the same length (Table II), which argues against a hyperconjugative interaction of this type that affects the geometry. Similarly it is unlikely that silicon acts as π acceptor,[23g] as electron donation from carbon orbitals to the d orbitals of silicon is now regarded to be unimportant.[23j] The high electropositive character of silicon is the major reason for the high stability of silylketenes. Kinetic measurements of the hydration of Me_3SiCH=C=O show that rates are accelerated in the acid- and-base catalyzed reactions relative to alkylketenes.[23k] These results are attributed[23k] to the ability of silicon to stabilize the polar transition states leading to $Me_3SiCH_2C^+$=O and Me_3SiCH=C(OH)O^- in the acid and base reactions, respectively.

Some bisketenes are known,[24] and **15** (R = Ph) has been observed by IR as an intermediate from photolysis of **16** (R = Ph) in THF solution.[24e] The 6-31G*//6-31G* calculations (Table I) indicate that for R = H **15** is a saddle point 1.6 kcal/mol more stable than the cisoid isomer **15a**, which is 8.5 kcal/mol less stable than **16**, which is an energy minimum. Because the calculations indicate that ketenes are stabilized relative to alkenes by electropositive substituents, this suggests that with an appropriate choice of R **15** may become more stable than **16**.



15 15a 16

Comparison of Substituent Effects on Ketenes and on β-Ethyl Carbocations. Substituent effects on the isodesmic stabilization energies of β-ethyl carbocations **17** have been obtained by using 6-31G* single point energy calculations on the geometry shown with a tetrahedral (109.47°) arrangement about the β-carbon and a trigonal planar (120°) arrangement at the α-carbon, and bond lengths from an optimized geometry with R coplanar with the trigonal carbon.[5o] Fixing of the geometry of **17** was done to prevent bridging by the substituent. These results show a curved dependence of SE on substituent electronegativity,[5o] and there is a correspondingly curved relationship between the SE($RCH_2CH_2^+$) and our SE(RCH=C=O) (Figure 3). The structural resemblance of carbocations **17** to ketenes **18** suggests a relationship between substituent stabilization energies for the two is plausible. The break in the curve suggests that stabilization of the carbocations is enhanced relative to that of the ketenes for the strong hyperconjugative donors Li, BeH, BH_2, Na, MgH, and AlH_2.



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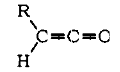

18

In summary 6-31G*//6-31G* calculations predict the effects of substituents on ketene structures and energies in good agreement with experimental data. A remarkably simple but accurate correlation between ketene stabilization, defined by the isodesmic reaction of eq 1, with group electronegativities is found. Thus ketenes are stabilized by electropositive groups, and there is also evidence for stabilization by π acceptor groups and destabilization by π donors.

Acknowledgment. Financial support by the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged. We thank Professor H. Bodenseh (Universitat Ulm) for unpublished results on cyanoketene (ref 8h), and Professor R. J. Boyd for the unpublished group electronegativities for CF_3 and c-Pr.

Supplementary Material Available: Tables of complete geometrical parameters and Z matrix data (41 pages). Ordering information is given on any current masthead page.

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