lactone **1** chemically, the photolysis was carried out in methanol. Irradiation of 0.1 *M* methanolic solutions of the cyclic peroxide at 350 nm and 35–40° in Pyrex test tubes afforded 2-*n*-butyl-2-methoxycaproic acid (**7**) as major product (88% yield as its methyl ester[20]), besides 5-nonanone (5.3%), di-*n*-butylmalonic acid (3.7% yield as its dimethyl ester[20]), and 2-*n*-butylhex-2-enoic acid (3% as its methyl ester[20]), giving a quantitative product balance. The α-methoxy acid **7** was identified by its physical constants and spectral data with an authentic sample, prepared by addition of *n*-butyl bromide and dimethyl oxalate to a magnesium and ether suspension in order to obtain methyl 2-*n*-butyl-2-hydroxycaproate,[21] methylation of the latter with sodium hydride and methyl iodide,[22] and finally saponification of the α-methoxy ester to give **7**. Control experiments demonstrated that the polyester **4** is not solvolyzed with methanol to give significant amounts of the α-methoxy acid **7** in the dark or under irradiation. There is, however, a dark reaction between the cyclic peroxide and methanol to give a complex product mixture,[23] but kinetic experiments show that during the time interval of the photolysis, at the very most 3–5% of solvolysis has taken place.

In summary, the mechanism of the photolysis (eq 2) of di-*n*-butylmalonyl peroxide (**2**) is proposed to involve photodecarboxylation to produce an α-lactone intermediate **1**. In hydrocarbon solvents such as hexane and benzene the dipolar α-lactone intermediate polymerizes into the polyester **4**; however, in a hydroxylic solvent such as methanol[24] this intermediate is trapped as α-methoxy acid (**7**). As a minor route, probably a carbene intermediate **3** is formed which is converted to 5-nonanone (**5**) and 4-nonene (**6**).[25] It is imperative that steric and/or electronic stabilization must be introduced in the α-lactone **1**, in order to enhance its lifetime.

Acknowledgments. Financial support by the A. P. Sloan Foundation, National Science Foundation, the Petroleum Research Fund, and the Research Corporation and a Fullbright travel grant to R. R. are gratefully appreciated. We thank Professor P. D. Bartlett (Harvard University) for releasing to us his results on related work[12] prior to publication.

(20) The product mixture was treated with diazomethane and submitted to glpc analysis on a Carbowax 20M column.

(21) H. Hepworth, *J. Chem. Soc. London*, **115**, 1206 (1919).

(22) U. E. Diner, F. Sweet, and R. K. Brown, *Can. J. Chem.*, **44**, 1591 (1966).

(23) The methanolysis of the malonoyl peroxide shall be the subject of a separate publication.

(24) Preliminary experiments indicate that ethyl alcohol, isopropyl alcohol, and *tert*-butyl alcohol also serve as trapping agents of the α-lactone intermediate.

(25) Alternatively, the ketone could be formed by photodecarbonylation of the α-lactone.

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Reactions of Sulfur Atoms. XII. Arrhenius Parameters for the Addition to Olefins and Acetylenes

Sir:

The reactions of ground-state S(^{3}P) atoms with olefins proceed *via* a stereospecific path resulting in the formation of the corresponding episulfide as the only principal product.[1] These reactions provide the only known example of a stereospecific path of a divalent triplet-state reagent. In order to elucidate details of the mechanism we have determined relative Arrhenius parameters for a representative series of olefins and acetylenes.

Ground-state S(^{3}P$_{2,1,0}$) atoms were generated by the direct photolysis of COS admixed with a large excess of CO$_2$ or by Hg(^{3}P$_1$) photosensitization[2] in the presence of known concentrations of two competing olefins. Relative rates as a function of temperature were obtained from the gas chromatographically determined yields of the two episulfides produced. The results are presented in Table I. Check experiments using direct photolysis or sensitization, varying the olefin concentrations, or using different pairs of olefins, a + b, b + c, or a + c, have led to concordant results. In cases where the primary reaction product was unstable (*e.g.*, acetylenes), rates were obtained from determining the suppressing effect of one of the olefins on the yields of the stable episulfide from the other olefin. A narrow temperature range, from 298°K to the thermal decomposition point, ~450°K, of the less stable product episulfide, was covered.

The trend in activation energies clearly manifests the electrophilic nature of attack by the sulfur atom; increasing the number of alkyl substituents on the doubly bonded carbons decreases E_a, while increasing the number of halogen substituents increases E_a. These variations can be correlated with molecular properties such as ionization potentials, excitation energies, and bond orders in a similar fashion as for O(^{3}P) atoms,[3] the CF$_3$ radical,[4] and other electrophilic reagents.[3] The activation energy for the ethylene reaction is 3.36 kcal larger than for the tetramethylethylene (TME) reaction. If the latter is zero or positive, then $E_a(C_2H_4) \geqslant 3.4$ kcal. The *A* factor for the ethylene reaction is 8.3-fold lower than that for the abstraction reaction

which in turn cannot be higher than a few tenths of the gas kinetic collision frequency. Thus, the upper limit for $A(C_2H_4)$ is $\leqslant 10^{10}$ l. mol^{-1} sec^{-1}. Therefore, the upper limit for $k(C_2H_4) = 10^{10}e^{-3{,}360/RT}$. At room temperature this leads to a value of 3.7×10^7 l. mol^{-1} sec^{-1}, while absolute measurements[5,6] give $(7–9) \times 10^8$ l. mol^{-1} sec^{-1}. The discrepancy can be resolved by assuming that the activation energy for the TME reaction has a negative value of 1.9 kcal, as discussed in the accompanying communication,[6] which results in $E_a(C_2H_4) = 1.5$ kcal.

Changes in the *A* factor require the involvement of at least two opposing effects. Of these, for alkyl substituents, steric repulsion seems to predominate. For

(1) H. E. Gunning and O. P. Strausz, *Advan. Photochem.*, **4**, 143 (1966).

(2) K. S. Sidhu, I. G. Csizmadia, O. P. Strausz, and H. E. Gunning, *J. Amer. Chem. Soc.*, **88**, 2412 (1966).

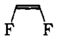
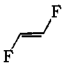
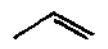
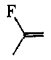
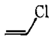
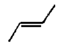
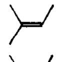
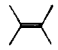
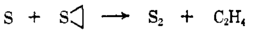
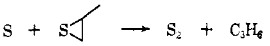
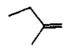
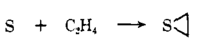
(3) R. J. Cvetanović, *Advan. Photochem.*, **1**, 115 (1963).

(4) J. M. Pearson and M. Szwarc, *Trans. Faraday Soc.*, **60**, 553 (1964); G. E. Owen, J. M. Pearson, and M. Szwarc, *ibid.*, **61**, 1722 (1965).

(5) R. J. Donovan, D. Husain, R. W. Fair, O. P. Strausz, and H. E. Gunning, *Trans. Faraday Soc.*, **66**, 1635 (1970).

(6) J. Connor, A. van Roodselaar, R. W. Fair and O. P. Strausz, *J. Amer. Chem. Soc.*, **93**, 561 (1971).

Table I. Arrhenius Parameters for the Addition of S($^3P_1$) Atoms to Olefins and Acetylenes and for the Abstraction of Sulfur from Episulfides

	$E_a(C_2H_4) - E_a$, kcal/mol	$A/A(C_2H_4)$		$E_a(C_2H_4) - E_a$, kcal/mol	$A/A(C_2H_4)$
C_2H_4	0.0	1.0		2.15	0.67
C_2D_4	0.0	1.14		−0.73	1.4
CD_2CH_2	0.0	1.07		−2.71	1.7
cis-CHD-CHD	0.0	1.04		−2.62	3.4
	1.14	1.0	C_2F_4	−1.4	1.4
	1.72	0.75		−1.5	1.2
	2.09	0.53		−0.52	3.4
	2.01	0.65	C_2H_2	−2.0	6.2
	2.36	0.97	$CH_3C{\equiv}CH$	−0.9	6.2
	3.01	0.51		1.3	2.7
	3.36	0.50		1.8	8.3
	2.04	2.4		2.1	8.4
	2.83	0.78		abs (7–9) × 10^8 l. mol^{-1} sec^{-1} at 298°K	

halogen atoms, the steric repulsion appears to be overcompensated for by an enhancing effect, the origin of which cannot be clearly established. The observed inverse secondary α-H/D kinetic isotope effect is temperature independent. According to absolute rate theoretical calculations it arises largely from the tightening of the out-of-plane CH bending vibrations due to the rehybridization of the carbon atoms during the passage from reactants to the activated complex. It is then possible that a heavy-atom substituent would similarly affect the A factor.

The acetylene reactions which are believed to afford the unstable thiirenes feature somewhat higher activation energies and considerably higher A factors than the olefin reactions. The trends with methyl substituents, however, remain; the activation energy decreases and the A factor falls off, in general agreement with the behavior of other electrophilic reagents.[4,7] Szwarc and coworkers[4] have attributed the large A factors of the acetylene reactions to a gain in the entropy of activation, as compared to the olefin reactions, in going from the linear acetylene to the nonlinear activated complex.

The primary product of the ethylene addition reaction has been postulated to be the lowest lying, symmetrical (n,σ^*) triplet or the vibrationally excited ground-state episulfide.[8] Recent *ab initio* MO calculations indicate the existence of a lower lying excited triplet state with a semiopen ring structure (∠SCC = 105°). This reaction path is spin allowed and may borrow intensity from the symmetry-allowed (n,σ^*) path, as suggested for the ground state by Hoffmann and coworkers.[8]

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(8) R. Hoffmann, C. C. Wan, and V. Neagu, *Mol. Phys.*, **19**, 113 (1970); *cf.* also E. Leppin and K. Gollnick, *Tetrahedron Lett.*, 3819 (1969).

The Addition of Group VIa Atoms to Tetramethylethylene. An Addition Reaction with a Negative Activation Energy

Sir:

The reactions of ground-state ($^3P_{2,1,0}$) atoms of the group VIa elements with olefins have received considerable attention in recent years.[1–7] Atomic oxygen yields epoxides, the isomeric carbonyl compounds, and various fragmentation products. Sulfur, selenium, and tellurium give only the cyclic adduct which, with the latter two elements, has only transient existence.

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(1) R. J. Cvetanovic, *Advan. Photochem.*, **1**, 115 (1963), and references therein.

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(5) A. B. Callear and W. J. R. Tyerman, *Trans. Faraday Soc.*, **62**, 371 (1966).

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