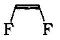
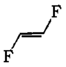
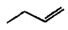
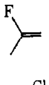
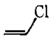
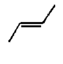
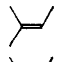
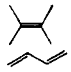
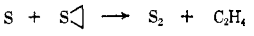
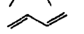
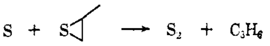
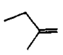
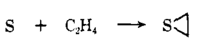
Table I. Arrhenius Parameters for the Addition of $S(^3P_1)$ Atoms to Olefins and Acetylenes and for the Abstraction of Sulfur from Episulfides

	$E_a(C_2H_4) - E_a$, 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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(7) A. A. Westenberg and N. deHaas, *J. Phys. Chem.* **73**, 1181 (1969); D. Saunders and J. Heicklen, *ibid.*, **70**, 1950 (1966); P. I. Abell, *Trans. Faraday Soc.*, **60**, 2214 (1964); D. G. Williamson and K. D. Boyes, *J. Amer. Chem. Soc.*, **90**, 1957 (1968); W. B. DeMore, *Int. J. Chem. Kinet.*, **1**, 209 (1969).

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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.

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

(3) E. M. Lown, E. L. Dedio, O. P. Strausz, and H. E. Gunning, *J. Amer. Chem. Soc.*, **89**, 1056 (1967), and references therein.

(4) O. P. Strausz, W. B. O'Callaghan, E. M. Lown, and H. E. Gunning, *J. Amer. Chem. Soc.*, **93**, 559 (1971).

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

(6) A. B. Callear and W. J. R. Tyerman, *ibid.*, **62**, 2760 (1966).

(7) J. Connor, G. Greig, and O. P. Strausz, *J. Amer. Chem. Soc.*, **91**, 5695 (1969).

For the oxygen atom reactions, Cvetanovic[1] proposed that the rate-determining step is the formation of a π complex which readily passes to a σ complex and the latter species undergoes ring closure, rearrangement, and fragmentation processes. However, Szwarc and coworkers[8,9] suggested that the formation of the σ complex is rate determining; any π complex formation occurs without an appreciable activation energy before the transition state is reached. It has generally been assumed that the overall activation energy of the reaction is positive. We have obtained absolute rate data for the addition of atomic sulfur and tellurium to olefins which necessitates some modification of the previously proposed potential energy surfaces.

The rate of addition of $Te(^3P_2)$ atoms to tetramethylethylene (TME) was determined using the flash photolysis of dimethyl telluride (DMT, 10^{-1}–10^{-3} Torr with CO_2 diluent) as the source of atoms.[7] Olefin photolysis was minimized by a water filter surrounding the reaction cell. A 15-mm thick filter was used at 25°; high-temperature data were obtained by circulating water at 80° through a 5-mm thick jacket. Spectra were recorded on Kodak 103a-O plates sensitized by sodium salicylate. The concentration of $Te(^3P_2)$ atoms was monitored from the intensity of the atomic line at 2143 Å for which the Beer–Lambert exponent is[7] 0.5 ±0.1.

The tellurium atom decay rate in flashed DMT + TME + CO_2 mixtures was corrected for reaction with DMT, which was determined in separate experiments and accounted for ~50% of the total decay rate. The data along with those for ethylene and propylene are given in Table I. The rate constants for the addition of $Te(^3P_2)$ to TME correspond to an activation energy of (−1.6 ± 1.4) kcal/mol. To our knowledge, this is the first reported case of a negative temperature coefficient for an addition reaction in its second-order region.

Table I. Reactions of $Te(^3P_2)$ Atoms

	k, l. mol^{-1} sec^{-1} [a]		E_a,
Substrate	25°	80°	kcal/mol
DMT	(1.65 ± 0.25)	(1.5 ± 0.2) × 10^{11}	
C_2H_4	(1.3 ± 0.3)	(2.4 ± 0.5) × 10^7	2.5
C_3H_6	(1.2 ± 0.3)	(1.4 ± 0.3) × 10^8	0.6
TME	(3.9 ± 0.8)	(2.6 ± 0.9) × 10^9	−1.6 ± 1.4

[a] Errors are standard deviations.

Rate constants for the addition of $S(^3P)$ atoms to ethylene, propylene, butene-1, *trans*-butene-2, isobutylene, and TME were determined at 25°. Flash photolysis of mixtures containing 0.1 Torr COS and 200 Torr CO_2 yielded $S(^3P_{2,1,0})$ atoms, the $S(^1D_2)$ atoms formed by the photolysis being rapidly quenched to the ground state by CO_2.[10] Spectra were recorded with a McPherson 225 vacuum uv spectrograph on Kodak SWR film. The atoms were detected by the transitions at 1807 ($^3P_2$), 1820 ($^3P_1$), and 1826 Å ($^3P_0$). Beer–Lambert exponents of the $^3P_2$ and $^3P_1$ lines were 0.5 ± 0.1, but the $^3P_0$ line was too weak for quantitative measurements. The $^3P_1$ atoms were found to be in equilibrium with the $^3P_2$ state atoms.

The decay of atomic sulfur in the presence of an olefin was attributed entirely to the addition reaction as the olefins increased the S decay rates by at least a factor of 10. Changing the flash energy demonstrated that the products of any olefin photolysis, with the possible exception of TME, did not affect the atomic decays. The results are summarized in Table II. The ethylene rate constant agrees well with the recently published value[11] of (7.2 ± 1) × 10^8 l. mol^{-1} sec^{-1}. The rate constants relative to that of ethylene are in satisfactory agreement with the values obtained from the relative Arrhenius parameters determined from conventional photolysis studies.[4]

Table II. Reactions of $S(^3P)$ Atoms at 25°

	$10^{-9}k$, l. mol^{-1} sec^{-1} [a]	$k/k_{C_2H_4}$ [b]	$k/k_{C_2H_4}$ [c]
Ethylene	0.9 ± 0.1	1.0	1.0
Propylene	6 ± 1	7.5 ± 1.3	6.7
Butene-1	9 ± 1	11 ± 2	12
trans-Butene-2	12 ± 2	15 ± 3	20
Isobutylene	36 ± 5	45 ± 6	52
TME	62 ± 8 [d]	77 ± 10	133

[a] Errors are standard deviations. [b] This work. For the C_2H_4 rate constant the mean of the present and previous values, 0.8, is used. [c] Reference 4. [d] Lower limit.

The reactivity of the group VIa atoms toward olefins is governed mainly by the activation energies which increase with increasing ionization potential of the olefin, the preexponential factors remaining fairly constant.[1,4,6] The literature values of the A factors for O + C_2H_4[12–14] and Se + C_2H_4[5] are (1.0 ± 0.5) × 10^{10} and (1.1 ± 0.4) × 10^{10} l. mol^{-1} sec^{-1}, respectively; the A factor for S + C_2H_4 therefore is probably (1.0 ± 0.5) × 10^{10} l. mol^{-1} sec^{-1}. That this is an upper limit has been shown in the accompanying article. This then leads to E_a = (1.5 ± 0.4) kcal/mol. Combining this with the value $E_a(S + C_2H_4) - E_a(S + TME) = 3.4$ kcal as derived from competitive rate studies,[4] the activation energy for the addition of $S(^3P)$ to TME is (−1.9 ± 0.4) kcal/mol. Alternatively, taking[4] $A(TME) = A(C_2H_4)/2 = 5 \times 10^9$ l. mol^{-1} sec^{-1}, E_a(TME) from the present measurement is −1.5 kcal/mol.

The activation energy of the reaction of $O(^3P)$ with TME is 2.6 kcal/mol lower[1] than that of O + C_2H_4 and is therefore[12–15] 1.5 − 2.6 = −1.1 kcal/mol. Extrapolation of Callear and Tyerman's plot[6] correlating the activation energies of the atomic selenium reactions with the ionization potential of the olefin involved indicates that E_a of Se + TME is also negative.

It would therefore appear that the activation energies of the reactions of all the group VIa atoms with olefins become negative when the olefin's ionization potential is sufficiently low. To account for this phenomenon, we suggest that the atom and olefin initially approach on

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(8) A. P. Stefani and M. Szwarc, *J. Amer. Chem. Soc.*, **84**, 3661 (1962).

(9) G. E. Owen, Jr., J. M. Pearson, and M. Szwarc, *Trans. Faraday Soc.*, **61**, 1722 (1965).

(10) H. A. Wiebe, A. R. Knight, O. P. Strausz, and H. E. Gunning, *J. Amer. Chem. Soc.*, **87**, 1443 (1965).

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

(12) L. Elias and H. I. Schiff, *Can. J. Chem.*, **38**, 1657 (1960).

(13) L. Elias, *J. Chem. Phys.*, **38**, 989 (1963).

(14) A. A. Westenberg and N. de Haas, *J. Phys. Chem.*, **73**, 1181 (1969).

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a potential surface with a shallow minimum. The repulsive part of this surface intersects an attractive potential surface and the crossing between the two surfaces is the rate-determining step of the reaction. A positive activation energy clearly corresponds to the crossing point lying at higher energies than the separated reactants. However, if the intersection lies below the separated reactants, an increase in temperature decreases the probability of crossing between surfaces due to the higher average velocity of the collision complex at the crossing point.[16] This is responsible for the negative temperature coefficient found in the reactions with tetramethylethylene.

Acknowledgment. We thank the National Research Council of Canada for financial support.

[16] V. N. Kondrat'ev, "Chemical Kinetics of Gas Reactions," Pergamon, London, 1964, p 217.

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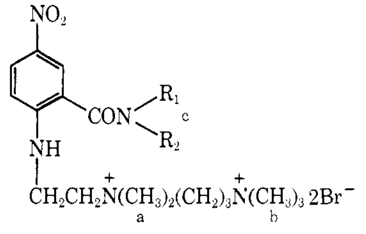
Topography of Nucleic Acid Helices in Solutions. Steric Requirements for Intercalation[1]

Sir:

It is well known that planar molecules such as acridine orange, ethidium bromide, proflavine, and actinomycin may intercalate between base pairs in DNA.[2] This phenomenon leads to an increase in the length of the helix and is usually accompanied by an increase in the viscosity of the solution. In order to delineate the steric requirements for the intercalation process, reporter molecules, I, with increasing size of R substituents were synthesized.[3]



1, $R_1 = R_2 = H$
2, $R_1 = CH_3; R_2 = H$
3, $R_1 = R_2 = CH_3$
4, $R_1 = R_2 = CH_2CH_3$

The results of the absorption and the induced circular dichroism studies of free and DNA-bound reporters are given in Table I. The temperature dependent partial proton magnetic resonance spectra are shown in Figure 1, and the results of the low-shear viscometric studies are given in Table II.

A number of interesting observations may be made. (1) The reporter molecules **1** and **2** where $R_1 = R_2 = H$ and $R_1 = H$, $R_2 = CH_3$, respectively, show a strong hypochromic effect (47 and 41%), and a large induced circular dichroism ($[\theta]^t = -6590$ and $-10{,}060$) of the 4-nitroaniline transition on binding to salmon sperm DNA (Table I). (2) Considerable broadening of the pmr signal of the a- and b-methyl protons of **1** and **2** are observed in the DNA complex at 32°.[4] In the case of DNA–**2** complex the pmr signal of the c-methyl protons is completely broadened and indistinguishable from base-line noise at 32 and 58°, indicating a restricted tumbling rate of the 4-nitroaniline ring of **2**. At 90°, where melting of the DNA helix has occurred,[5] sharp resonance lines characteristic of the free reporter molecules are observed for the a-, b-, and c-methyl protons. More rapid tumbling and/or efficient averaging of the chemical-shift environment is indicated. (3) The low-shear viscometric studies show that the intrinsic viscosity of the DNA-bound reporters **1** and **2** relative to free DNA are increased by 0.26 and 0.30, respectively (Table II). The above results, 1, 2, and 3, are strongly suggestive that the 4-nitroaniline ring of reporters **1** and **2** is intercalated between base pairs in DNA. This is

Table I. Effect of Salmon Sperm DNA (ss DNA) on the Absorption and Induced Circular Dichroism Spectra of Reporter Molecules **1–4**[a]

	Absorption spectra					Circular dichroism	
	H₂O–buffer		ss DNA			ss DNA	
Reporter	λ^{max}, nm	ϵ^{max}	λ^{max}, nm	ϵ^{max}	% H[b]	λ^t, nm	$(\theta)^t \times 10^{-3}$
1	373	16,190	389	11,000	47.0	385	−6.59
2	374	14,770	393	10,450	41.0	395	−10.06
3	372	13,650	375	13,540	1.0	360–400	0.34
4	372	12,140	374	11,500	5.6	360–400	0.40

[a] At 25.0 ± 0.2° in 0.01 *M* sodium phosphate buffer, pH 6.40–6.50 (0.01 *M* in Na^+). Spectra were taken in 10-mm cells using Cary 14 and Cary 60 spectrometers. Values of λ^{max}, ϵ^{max}, λ^t, and $(\theta)^t$ in the presence of nucleic acid reported in this table are limiting values, *i.e.*, additional change in spectra is not observed at further excess of nucleic acid. [b] Percentage hypochromicity (% H) = $[\epsilon_{H_2O}^{max}/\epsilon_p^{max} - 1.00]100$, where $\epsilon_{H_2O}^{max}$ and ϵ_p^{max} are the extinction coefficients in the presence and absence of the polynucleotides.

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[1] This is related (as XXII) to other articles on Topography of Nucleic Acids in Solutions. For part XXI, see E. J. Gabbay, B. Gaffney, and R. Glaser, *Ann. N. Y. Acad. Sci.*, **171**, 810 (1970).

[2] (a) L. S. Lerman, *J. Mol. Biol.*, **3**, 18 (1961); (b) D. S. Drummond, N. J. Pritchard, V. F. W. Simpson-Gildemeister, and A. R. Peacocke, *Biopolymers*, **4**, 971 (1966); (c) G. Cohen and H. Eisenberg, *ibid.*, **8**, 45 (1969); (d) W. Müller and D. M. Crothers, *J. Mol. Biol.*, **35**, 251 (1968).

[3] The reporter molecules **1–4** were prepared according to the procedure of E. J. Gabbay (*J. Amer. Chem. Soc.*, **91**, 5136 (1969)) and analyzed by ir, pmr, uv, and elemental analysis.

[4] If the rate of molecular tumbling of molecules in solutions is lower than the typical Larmor frequencies W_0 (of the order of 10^8–10^9 radians sec^{-1} for protons in the conventional magnetic field), then T_2, the transverse relaxation time, is considerably diminished, leading to substantial line broadening of the proton signal (see O. Jardetsky and C. D. Jardetsky in "Methods of Biochemical Analysis," D. Glick, Ed., Interscience, New York, N. Y., 1962). This situation is obtained if the proton is contained in a rigid macromolecule, *e.g.*, DNA, or if the proton is contained in a slowly tumbling small molecule bound to a macromolecule.

[5] Evidence for the melting of DNA is seen in Figure 1 by the appearance of the thymine methyl peaks at 1.5–2.0 ppm [C. C. McDonald, W. D. Phillips, and J. Lazar, *J. Amer. Chem. Soc.*, **89**, 4166 (1967)].