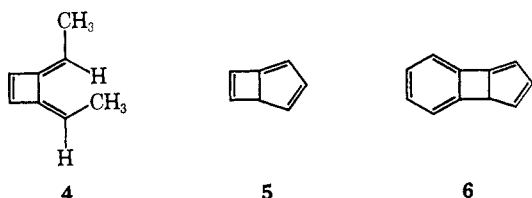
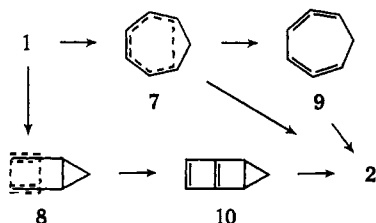


8.22 (3 H).⁸ This compares very favorably with the spectrum of a model bismethylenecyclobutene **4**, which shows⁸ pmr absorption at τ 3.13, 3.30, 4.74, 5.02, 8.21, and 8.27.

Triene **2** is a colorless oil which solidifies at -78° . Although it reacts rapidly with oxygen and polymerizes at a moderate rate in neat form, nmr concentrations of **2** ($\sim 0.5 M$) are stable for several days at 0° under an inert atmosphere. This contrasts with the fact that both its double-bond isomer **5** and the corresponding benzo derivative **6** dimerize immediately upon generation in solution.^{1a-c}



The most reasonable first bond-formation transition state for the **1** \rightarrow **2** isomerization appears to be either **7** or **8**. These species differ primarily in their extent of 1,5 bonding; both appear to be highly strained. Whether any of the diastereomers of cyclic bisallene **9** or fused cyclobutadiene **10** constitute minima on the energy surface leading to **2** remains conjectural.



Efforts are now under way aimed at converting **2** to spectrally observable concentrations of a number of fully conjugated bicycloheptatrienyl systems, and at applying the **1** \rightarrow **2** reaction type in the synthesis of heterocyclic compounds isoelectronic with these derivatives.

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(8) All couplings in the molecule are small and there seems to be some long-range coupling, resulting in broadening of the vinyl proton lines. The methyl group appears to be a four-line pattern due to coupling with the methylene hydrogens ($J \cong 0.5-1.0$ Hz) and one of the cyclobutene hydrogens ($J \cong 0.5-1.0$ Hz). The methylene hydrogens appear to be coupled to the 5-ring vinyl proton ($J \cong 2$ Hz) as well as to the methyl group.

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The Reactions of Tellurium Atoms. I

Sir:

The atomic reactions of the group VIA elements oxygen,^{1,2} sulfur,³ and selenium⁴⁻⁷ have been exten-

- (1) F. Kauffman, *Progr. Reaction Kinetics*, **1**, 1 (1961).
(2) R. J. Cvetanović, *Advan. Photochem.*, **1**, 115 (1963).

sively studied, but little work has been done on the reactions of tellurium atoms. Tellurium atoms and tellurium alkyls have been known to be antiknocks for some time. Callear and Norrish⁸ detected the presence of Te atoms in investigations of the antiknock properties of dimethyl telluride; however, no investigation of the atomic reactions was made. In recent flash photolysis studies we found that the uv photolysis of dimethyl telluride (DMT) is a usable source of $^3P_{2,1,0}$ tellurium atoms.

The uv absorption spectrum of DMT indicates two major systems, one with a maximum at 2500 Å, the other at 2000 Å. The absorption at shorter wavelengths shows considerable structure while that at longer wavelengths displays additional maxima at 2425 and 2575 Å. With the quartz reaction vessels used, absorption took place in both systems.

In flashed mixtures of DMT vapor (10^{-3} – 10^{-1} Torr with CO₂ diluent) using kinetic absorption spectroscopy, we observed intense atomic absorptions at λ 2143 and 2259 Å corresponding to known transitions of Te(3P_2) and at 2386 and 2383 Å corresponding to Te(3P_1) and (3P_0), respectively. Several molecular systems were also observed. One appearing between 3600 and 4300 Å corresponds to that assigned to the Σ – Σ type transition of the Te₂ molecule;⁹ another, a regular progression of eight bands between 2750 and 2850 Å, has not yet been assigned. At low initial pressures of DMT, the 2160-Å absorption of the CH₃ radical was detected.

From flash energy variations, the carrier of a series of four bands between 2240 and 2430 Å appears to be a primary photoproduct, very likely the CH₃Te radical. The appearance of another system in the same region follows the decay of CH₃Te closely. More precise kinetic studies are being undertaken in an attempt to clarify the origin of these systems.

In the presence of added ethylene two further band systems have been observed. The system between 2400 and 2500 Å (band heads at 2472, 2410, and possibly at 2356 Å) has a lifetime of several milliseconds and has been assigned to the unstable ethylene epitelluride molecule. The other system around 2300 Å decays faster (~ 250 μ sec) in an apparent first-order process. Analogous spectra (at 2480 and 2458 Å) have also been obtained with added propylene.

The formation of transient epitelluride molecules has been confirmed by kinetic mass spectrometry. The flash photolysis-kinetic mass spectrometry apparatus has been described in earlier communications.^{10,11} Flashing 0.2 Torr of DMT in the presence of 10 Torr of propylene, the parent adduct C₃H₆Te (m/e 172) has been detected. At this mass number there was no inter-

(3) H. E. Gunning and O. P. Strausz, *ibid.*, **4**, 143 (1966).

(4) A. B. Callear and W. J. R. Tyerman, *Trans. Faraday Soc.*, **61**, 2395 (1965).

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

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

(7) W. J. R. Tyerman, W. B. O'Callaghan, P. Kebarle, O. P. Strausz, and H. E. Gunning, *J. Am. Chem. Soc.*, **88**, 4277 (1966).

(8) A. B. Callear and R. G. W. Norrish, *Proc. Roy. Soc.*, **A259**, 304 (1960).

(9) B. L. Jha and D. Ramchandra Rao, *Chem. Phys. Letters*, **3**, 175 (1969).

(10) O. P. Strausz, J. Font, E. L. Dedio, P. Kebarle, and H. E. Gunning, *J. Am. Chem. Soc.*, **89**, 4805 (1967).

(11) W. J. R. Tyerman, M. Kato, S. Masamune, O. P. Strausz, and H. E. Gunning, *Chem. Commun.*, 497 (1967).

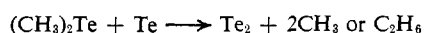
ference from the cracking pattern of the parent DMT. In 50 msec little decay had taken place.

The addition of ground-state tellurium atoms to olefins to form short-lived adducts resembles the behavior of selenium atoms which also form short-lived adducts with olefins.⁴⁻⁷

Some quantitative rate measurements were also carried out. Relative concentrations of Te(³P₂) atoms were estimated by photometry of the 2143- and 2259-Å absorption lines. A Beer-Lambert factor of 0.5 ± 0.1 has been established for the atomic transitions, relating changes in optical density to atomic concentrations.

Atomic decay has been investigated with various chaperons in the pressure range 30-300 Torr. Hydrogen, CH₄, and *i*-C₄H₁₀ were found to be efficient in bringing about spin-orbit relaxation of excited atoms,¹² while O₂, CO₂, and Ar were much less efficient. The excitation energies of the ³P₀ and ³P₁ states of Te are 4707 and 4751 cm⁻¹, respectively, and since ω_e for H₂ is 4395 cm⁻¹, the high relaxation efficiency of H₂ may be attributed to a resonance effect.

The decay of ground-state atoms has been found to be first order in all cases studied and the rate (in the absence of olefins) to be dependent on the concentration of DMT. Plate photometry showed the concentration of DMT to be constant throughout the atomic decay and was used to estimate the absolute concentration. A plot of the first-order rate constant in a variety of inert gases against DMT pressure during the decay was found to be a straight line passing through the origin. The second-order rate constant obtained was 1.7×10^{11} l. mole⁻¹ sec⁻¹. This corresponds to a reaction between tellurium atoms and DMT at virtually every collision. The reaction implied would appear to be



or the formation of an intermediate adduct which may then decompose to these products.

The presence of an olefin accelerates the atomic decay. From the observed rate increase it was possible to derive rate constants for the addition reactions, olefin

(12) Te(³P) atoms would not be expected to attack paraffins or hydrogen, and no evidence has been found for such reactions.

+ Te → epitelluride, for ethylene and propylene. These, along with the corresponding values for other members of the group, are shown in Table I. All rate

Table I

	O(³ P)	S(³ P)	Se(³ P)	Te(³ P)
$k_{\text{C}_2\text{H}_4}$	3×10^{10a} 6×10^{10b}	7×10^{10c}	1×10^{10e}	2×10^7
$k_{\text{C}_2\text{H}_6}/k_{\text{C}_2\text{H}_4}$	5.8 ^a	6.8 ^d	3.5 ^e	10

^a Reference 2. ^b Reference 13. ^c Reference 14. ^d Reference 3. ^e References 4-7.

constants are in units of l. mole⁻¹ sec⁻¹. From the data, the Te atom addition is somewhat slower than the addition of O, S, or Se atoms and it is also more selective.

As an alternative source of tellurium atoms the flash photolysis of H₂Te has been briefly examined. Ground-state and spin-orbit excited Te atoms were observed along with Te₂. The 2750-2850-Å band progression was absent. A new transient species absorbing at about 2155 Å has been detected. The spectrum shows considerable rotational fine structure and may be due to the TeH radical.

Both first- and second-order plots of the atom decay showed curvature consistent with a transition from an initial second-order process for the removal of atoms to a first-order process.

A standard flash photolysis apparatus was employed. Spectra were recorded with a medium quartz spectrograph on Kodak 103a-O plates sensitized for the far-uv by sodium salicylate and developed for 4 min in Kodak D19 developer. Plates were photometered on a Joyce-Loebl Mark III recording microdensitometer.

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

(14) R. J. Donovan, unpublished results.

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Additions and Corrections

Structure of Chlorophyll *c* [*J. Am. Chem. Soc.*, **88**, 5037 (1966)]. **Structure of Phycocyanobilin** [*J. Am. Chem. Soc.*, **89**, 3642 (1967)]. **A Perturbation Molecular Orbital Approach to the Interpretation of Organic Mass Spectra. The Relationship between Mass Spectrometric, Thermolytic, and Photolytic Fragmentation Reactions** [*J. Am. Chem. Soc.*, **90**, 5780 (1968)]. **Application of the Perturbation Molecular Orbital Method to the Interpretation of Organic Mass Spectra. The Hexahelicene Rearrangement and Other Electrocyclic Mass Spectrometric Reactions** [*J. Am. Chem. Soc.*, **90**, 5788 (1968)]. **Negative Ion Mass Spectra of Benzene, Naphthalene, and Anthracene. A New Technique for**

Obtaining Relatively Intense and Reproducible Negative Ion Mass Spectra [*J. Am. Chem. Soc.*, **90**, 6570 (1968)]. By R. C. DOUGHERTY, *et al.*, Evans Laboratory of Chemistry, The Ohio State University, Columbus, Ohio 43210.

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Synthesis of Sugar-like Phosphates by the Oxyphosphorane Condensation. Reaction of Glyoxal with Trialkyl Phosphites and Preparation of Phosphate Esters