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Mercury 6($^3P_1$) Photosensitization of Trifluoroethylene. A Source of the Difluorovinylidene Carbene

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Abstract: The triplet mercury photosensitization of trifluoroethylene proceeds via an excited molecule mechanism leading to the geminal molecular elimination of HF and the novel difluorovinylidene carbene with a zero-pressure extrapolated quantum yield of ≥ 0.8. An additional minor primary step is C=C bond cleavage giving :CF_2 and :CFH. Decomposition probably occurs from the excited triplet state of C_2HF_3, and the ethylidene structure is not implicated in the mechanism. Difluorovinylidene is formed in its singlet ground state and adds readily across the double bond of the parent olefin to give a hot difluoromethylene–trifluorocyclopropane which decomposes to :CF_2 + CF_2=C=CHF or, if partially pressure stabilized, isomerizes to CF_2=CHCF=CF_2. Difluorovinylidene also reacts with paraffins via direct insertion into the C–H bond but does not react with molecular oxygen or carbon monoxide.

In a previous publication on the Hg6($^3P_1$) photosensitized decomposition of mono- and difluorinated ethylenes,[2] it was shown that decomposition proceeds via an excited molecule mechanism by molecular elimination of HF. From a comparison of the experimental rate constants for the isomerization and decomposition reactions of ethylene, vinyl chloride, mono-, di-, and trifluoroethylenes with those computed with the aid of the RRK formula, it was concluded that intervention of the isomeric ethylidene structure in the decomposition mechanism is possible in all cases except with trifluoroethylene and 1,2-difluoroethylene. The estimated energy levels of the triplet ethylidene states of these latter molecules would lie so high that the rate constant for triplet ethylene → triplet ethylidene isomerization would be lower than the experimental rate constant for the overall decomposition. The RRK calculations employed were based on an empirical estimate of the triplet ethylene and ethylidene state energy levels derived from extended Hückel MO calculations.

The present article reports the determination of the experimental rate constant for the overall decomposition of trifluoroethylene and discusses the mechanistic details of the reaction.

Experimental Section

The apparatus and general experimental technique employed were similar to those described in the previous article.[2] Trifluoroethylene (Peninsular) was distilled from ethyl chloride slush (−139°) and purified by gas chromatography. O_2 and CO were Airco Assayed Reagent Grade and were used without purification. Propane-d_8 and cyclohexane-d_{12} were from Merck, C_3H_8 and CF_4 from Matheson, and cyclohexane from Phillips. They were degassed and purified by low-temperature distillation.

Analyses of the reaction mixtures were accomplished by combination of low-temperature distillation and gas-chromatographic separation. The reaction mixtures from the pure C_2HF_3 experiments were analyzed on a 28-ft 10% diisodecyl phthalate on Diatoport column at 25°. The substrate and C_2 products were trapped from the effluent and quantitatively analyzed on a 4-ft high-activity silica gel column at 50°. In experiments with added CF_4, the excess CF_4 was removed by distillation at liquid oxygen temperature (−183°). Similarly, with added O_2 or CO, the excess noncondensables were removed by pumping at −196°, and the reaction mixture was analyzed as above. In experiments with added propane, the analysis was accomplished as with pure C_2HF_3. In the case of added cyclohexane, the C_2 and C_3 compounds were distilled from the reaction mixture at −130° and analyzed as before. The remainder, consisting of the added cyclohexane and new reaction products, was analyzed on a 6-ft 20% di-*n*-nonyl phthalate on firebrick column at 25°.

Results

The products found were 1,1,2,4,4-pentafluorobutadiene (C_4HF_5), trifluoroallene (C_3HF_3), and tetrafluoroethylene (C_2F_4). C_2F_4 was identified by mass spectrometry. The mass spectrum of C_3HF_3, compiled in Table I, gave a large parent peak at *m/e* 94, and the ir spectrum, shown in Figure 1a, had a strong absorption band at 2040 cm^{-1}, the usual region for allenic type C=C stretching. The ir spectrum of 1,1-difluoroallene[3] also has a strong band at 2040 cm^{-1}. The NMR spectrum of C_3HF_3 exhibited two doublets, removed from one another by 87 Hz, with a splitting within the doublets of ca. 1 Hz. It is known that geminal H–F coupling in olefinic systems is very large, for example, 84.8 Hz in *cis*-1-fluoro-1-propane.[4] The small splitting is due to long range coupling to the fluorines on the other end of the molecule. Any other isomer of empirical formula C_3HF_3 would have exhibited a singlet or a triplet spectrum. The chemical shift of τ 2.92 is in the aromatic proton region, which is consistent with the shift to lower than normal field due to the presence of geminal fluorine.

Identification of the C_4HF_5 product was considerably more difficult. High-resolution mass spectra (Table I) were obtained at four different electron energies. From the varia-

Table I. Mass Spectra of the Trifluoroallene and 1,1,2,4,4-Pentafluorobutadiene Products from the Hg* + C_2HF_3 Reaction

m/e	Assignment	Relative intensity 70 eV	20 eV	15 eV	10 eV
C_3HF_3[a]					
94*	C_3HF_3	100			
44	C_2HF	33			
31	CF	31			
75	C_3HF_2	27			
56	C_3HF	13			
64	$C_2H_2F_2$ (impurity)	10			
50	CF_2	9			
93	C_3F_3	9			
74	C_3F_2	9			
95	$C_3H_2F_3$	8			
$CF_2{=}CHCF{=}CF_2$[b]					
75	C_3HF_2	100.0	100.0	100.0	100.0
31	CF	16.6	3.4		
93	C_3F_3	14.9	12.4	9.8	6.5
94	C_3HF_3	12.9	18.4	21.9	21.7
144*[c]	C_4HF_5	11.6	15.1	18.4	29.0
69	CF_3	4.4	3.4		
106	C_4HF_3	3.9	5.1	5.3	10.5
76	$C_3H_2F_2$	3.5	3.4	3.5	3.3
74	C_3HF_2	3.5			
56	C_3HF	3.2			
44	C_2HF/CO_2	3.2			
51	CHF_2	2.9			
125	C_4HF_4	2.6			
50	CF_2	2.5			
55	C_3F	2.1			
124	C_4F_4	1.9			
114	$C_3H_2F_4$	1.9	2.7	3.5	5.8
64	$C_2H_2F_2$	1.9			
95	$C_3H_2F_3$	1.6			
113	C_3HF_4	1.3			

[a] Taken with a Metropolitan Vickers M5-2 spectrometer. [b] Taken with an AE1 MS-9 high-resolution spectrometer. [c] Found: 143.9995; calculated: 143.9998. *Parent ions.

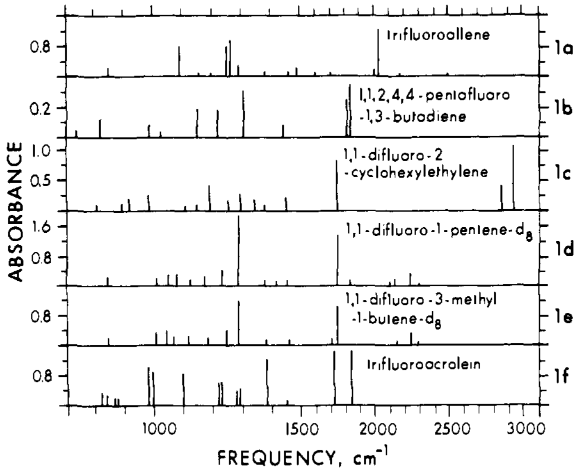


Figure 1. Schematic illustration of the ir spectra obtained in the gas phase with a Perkin-Elmer 421 spectrometer for the products trifluoroallene, 1,2,2,4,4-pentafluoro-1,3-butadiene, 1,1-difluoro-2-cyclohexylethylene, 1,1-difluoro-1-pentene-d_8, 1,1-difluoro-3-methyl-1-butene-d_8, and trifluoroacrolein.

Table II. Quantum Yields of Products from the Hg* + C_2HF_3 Reaction as a Function of C_2HF_3 Pressure[a]

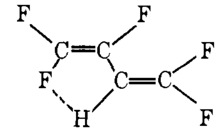
C_2HF_3 Pressure, Torr	Exposure time, min	$1/f$[b]	$\phi(C_2F_4)$	$\phi(C_3HF_3)$	$\phi(C_4HF_5)$
6.6	42.0	1.494		0.574	0.009
12.9	24.0	1.247		0.550	0.008
21.1	27.5	1.148		0.496	0.014
20.6	25.0	1.152	0.288		
32.2	25.0	1.101		0.452	0.020
51.3	35.0	1.056		0.355	0.031
52.0	23.0	1.055	0.218		
90.2	29.9	1.024		0.256	0.051
87.2	30.0	1.036	0.138		
133.0	93.0	1.017		0.139	0.046
173.0	80.0	1.011	0.066		

[a] I_a = 0.235 μeinstein/min, temp = 25 °C. [b] Lorentz broadening correction factor, determined as described in ref 2.

tion of relative peak intensities and the appearance of the two metastable ions, one at M* = 39.06 ($C_4HF_5^+ \rightarrow C_3HF_2^+ + CF_3$) and the other at M* = 60.00 ($C_3HF_3^+ \rightarrow C_3HF_2^+ + F$), it was possible to deduce that at least 90% of the spectrum is due to a structure having an empirical formula C_4HF_5. The exact mass of the 144 parent peak was 143.9995, while the calculated value is 143.9998. The peak at m/e 114, which corresponds to $C_3H_2F_4$ is likely a parent as well, but it cannot consist of more than 10% of the sample and likely much less. In related work[5] it has been found that tetrafluoropropylenes give large parent peaks at 114, and the impurity in the present spectrum was probably one of those.

The ir spectrum of C_4HF_5 (Figure 1b) exhibited two strong bands at 1827 and 1805 cm^{-1}, as well as strong bands in the region 1100–1300 cm^{-1}. The two bands above 1800 cm^{-1} are in the C=C stretching region commonly found for highly fluorinated dienes.[6] Since two strong bands are found, structures other than dienes, such as a methylene cyclopropane, can be ruled out.

The NMR spectrum could not be interpreted on a first-order basis. It consisted of two octets, separated by 65.93 Hz, the splitting within the octets being approximately constant at 3.2 Hz. The intensity ratios were ca. 1:1:3:3:3:3:1:1, which appear to be a quartet split into doublets. This, however, is not consistent with the structure mentioned above if the spectrum is normal first order. It is not surprising, on the basis of literature evidence[7] on the strength and role of H–F hydrogen bonding and the role that throughspace coupling plays in the NMR spectra of fluorocarbons,[8] that several anomalities would be found in the spectrum of a compound having the proposed structure:



At high-light intensities and conversions, formation of a solid polymeric material was also observed.

An additional very minor product was 1,1-difluoroethylene, identified only by its GC retention time. The 1,2-isomer appeared to be absent.

To examine the effect of pressure on product yields, two series of experiments were carried out. In series 1, the substrate pressure was varied between 6 and 175 Torr, and in series 2, the C_2HF_3 pressure was kept constant at 20 Torr and CF_4 added up to 100 Torr. The results are presented in Tables II and III and shown graphically in Figure 2. All quantum yield values are corrected for pressure broadening using the formula: $1/f = 0.992 + 2.94/P(\text{Torr})$ which was determined as described in ref 2. It is seen that the data in the two series overlap, indicating that the pressure effect observed is due entirely to collisional quenching of excited trifluoroethylene molecules. It is also to be noted that the yield of C_3HF_3 is equal to twice that of C_2F_4 except at low-substrate pressures, where some loss of C_3HF_3 may occur

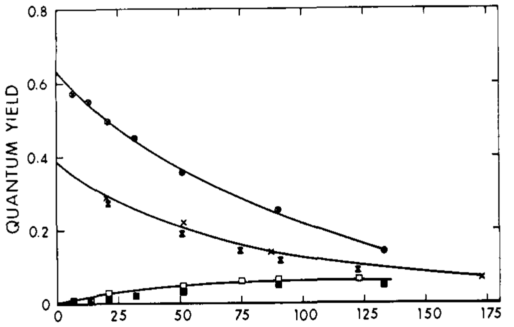


Figure 2. Quantum yields of C_3HF_3, ⊗, C_2F_4, **Ӿ** and ×, and C_4HF_5, □ and ⊠ as a function of total pressure: series 1, ⊗, ×, □; series 2, **Ӿ**, ⊠.

by photolysis or polymerization. The C_4HF_5 product evidently requires pressure stabilization as indicated by its rising yield with increasing pressure.

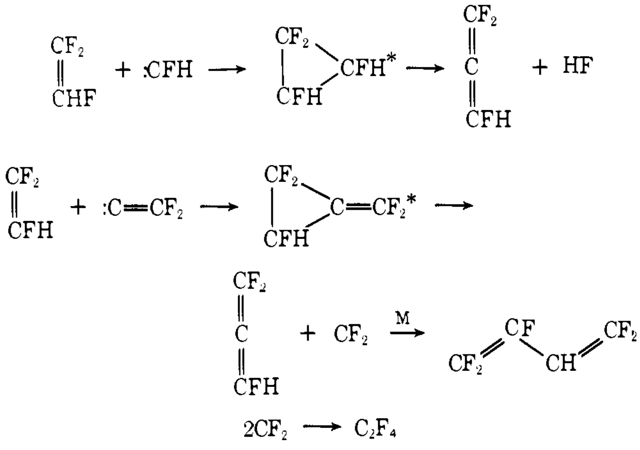
The stoichiometric equations for the formation of the observed products are

$$2C_2HF_3 \rightarrow C_3HF_3 + HF + CF_2(\tfrac{1}{2}C_2F_4)$$

$$2C_2HF_3 \rightarrow C_4HF_5 + HF$$

Thus, C_3HF_3 formation requires insertion of a carbon atom into the carbon-carbon double bond of C_2HF_3, and C_4HF_5 is formed by addition of a C_2F_2 entity to C_2HF_3. For the reactive intermediates, two reasonable alternatives appear, CHF from the primary decomposition $CF_2{=}CHF^* \rightarrow$ $:CF_2$ + $:CFH$ and $CF_2{=}C:$ from the primary decomposition $CF_2{=}CFH \rightarrow CF_2{=}C: + HF$. These carbenes could then give rise to the formation of final products via Scheme I.

Scheme I



In order to distinguish between these possibilities scavenging experiments were carried out with cyclohexane and cyclohexane-d_{12}. At low conversions, only one new product appeared. Comparison of the mass spectra from the deuterated and undeuterated systems allowed an assignment of the various fragments to be made and established the molecular formulas as $C_8H_{12}F_2$ and $C_8D_{12}F_2$. The most intense peak in the spectrum corresponded to a $C_4H_4F_2^+$ fragment analogous to the fragmentation of vinylcyclohexane.

This assignment was corroborated by the ir spectrum (Figure 1c) in that the compound $C_8H_{12}F_2$ exhibited strong absorption at 1740 cm^{-1}, corresponding to the stretching frequencies of the C=C bond in difluoroolefins.

Table III. Quantum Yields of Products from the Hg* + C_2HF_3 Reaction as a Function of Added CF_4 Pressure[a]

Pressure, Torr		Exposure time, min	$1/f$[b]	$\phi(C_2F_4)$[c]	$\phi(C_4HF_5)$	$\phi(C_4HF_5)/2\phi(C_2F_4)$
C_2HF_3	CF_4					
21.08	0.0	222.0	1.131	0.274	0.022	0.040
21.73	29.16	130.0	1.050	0.186	0.045	0.122
21.10	53.17	132.0	1.032	0.143	0.059	0.207
21.17	69.34	132.0	1.024	0.117	0.064	0.272
21.55	100.97	175.0	1.016	0.090	0.064	0.353

[a] I_a = 0.026 μeinstein/min, temp = 25 °C. [b] Lorentz broadening correction factor, determined as described in ref 2. [c] Trifluoroallene yields were not measured.

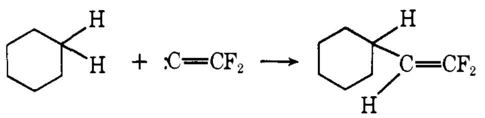
Table IV. Mass Spectra of the 1,1-Difluoro-3-methyl-1-butene-d_8 and 1,1-Difluoro-1-pentene-d_8 Products from the Reaction of $CF_2{=}C:$ with C_3D_8[a]

m/e assignment		Relative intensity		Assignment	m/e
$(CD_3)_2CDCD{=}CF_2$				$CD_3(CD_2)_2CD{=}CF_2$	
96	$C_4D_5F_2$	100	100	$C_3D_3F_2$	80
75	C_4D_4F	32	32	C_3D_6	48
30	C_2D_3	17	21	C_2D_3	30
54	CD_2F_2/C_4D_3	16	20	CDF_2/C_3D_8	52
114[b]	$C_5D_8F_2$	16	14	$C_5D_8F_2$	114[b]
42	C_3D_3	11	14	C_2D_5	34
46	C_3D_5	9	13	C_3D_5	46
68	$C_2D_3F_2$	8	10	C_3D_3	42
50	CF_2/C_3D_7	7	5	$C_3D_4F_2$	82
52	CDF_2/C_3D_8	7	5	$C_4D_5F_2$	96
66	$C_2D_2F_2$	6			

[a] Spectra were taken in a Metropolitan-Vickers MS-2 spectrometer at 70 eV. [b] Parent ion.

The NMR spectrum provided conclusive proof for the 1,1-difluoro-2-cyclohexylethylene structure. The spectrum of the ring hydrogens was split into two broad groups manifesting a fixed conformation, and that of the single olefinic hydrogen consisted of two triplets centered at τ 6.01. This chemical shift is normally outside the range of olefinic-hydrogen resonances (τ 4-5), indicating the presence of fluorine atoms across the double bond. If a fluorine atom had resided on the same carbon atom as the hydrogen atom, a shift in the opposite direction (ca. τ 3) would have occurred. The product is thus identified as 1,1-difluoro-2-cyclohexylethylene.

The precursor responsible for the formation of this product is the difluorovinylidene carbene $CF_2{=}C:$, and the mechanism involves a concerted insertive-type attack upon the C-H bonds:



Evidence for this mechanism is the complete absence of free radical recombination products such as bicyclohexyl and also the observation that small concentrations of added nitric oxide do not influence the yield of $C_8H_{12}F_2$.

Further studies on the scavenging reaction were carried out using propane-d_8. Two new products were found in this system. From mass spectrometric analysis (Table IV), it was concluded that they are isomers having an empirical formula $C_5D_8F_2$. The ir spectra (Figures 1d and e) showed a strong $C{=}CF_2$ stretching band at 1735 cm^{-1}, as well as the C-D stretching bands. Evidently the compounds were isomeric alkyl-substituted 1,1-difluoroethylenes. The cracking patterns from their mass spectra allowed an assignment of the structures. One of the isomers gave as the most intense peak a fragment resulting from CD_3 loss from the allylic position and was assigned the structure 1,1-difluoro-3-

Table V. Quantum Yields of Products from the Hg* + C_2HF_3 + C_3D_8 Reaction as a Function of C_3D_8 Pressure[a]

Pressure, Torr		Exposure							$\phi(CD_3CD_2CD_2CD{=}CF_2)$
C_2HF_3	C_3D_8	time, min.	$1/f$[b]	$1/Q$[c]	$\phi(C_2F_4)$	$\phi(C_3HF_3)$	$\phi(C_4HF_5)$	$\phi(C_5D_8F_2)$	$\phi((CD_3)_2CDCD{=}CF_2)$
20.5	0.0	40.0	1.136	1.000	0.277		0.015		
21.2	1.3	40.0	1.119	1.002	0.212		0.014	0.088	1.39
20.1	4.1	45.0	1.114	1.008	0.169		0.010	0.195	1.41
20.2	6.9	45.0	1.101	1.013	0.137		0.009	0.245	1.38
21.2	12.3	40.0	1.080	1.022	0.088		0.007	0.299	1.37
20.3	12.8	75.0	1.095	1.023	0.086	0.165	0.006	0.304	1.36
20.0	24.1	61.0	1.073	1.045		0.110	0.006	0.325	1.36
21.4	46.1	50.0	1.049	1.080				0.297	1.40
21.9	85.0	54.0	1.033	1.144				0.223	1.39
21.9	134.0	64.0	1.024	1.228				0.162	1.45
21.7	244.0	32.0	1.016	1.417				0.094	1.76

[a] I_a = 0.235 μeinstein/min, temp = 25 °C. [b] Lorentz broadening correction factor. [c] Competitive quenching correction factor calculated from $\sigma^2(C_3D_8)$ = 0.5 Å^2 and $\sigma^2(C_2HF_3)$ = 16 Å^2.

Table VI. Quantum Yields of Products from the Hg* + C_2HF_3 + C_3D_8 Reaction as a Function of C_2HF_3 Pressure[a]

Pressure, Torr		Exposure						
C_2HF_3	C_3D_8	time, min	$1/f$[b]	$1/Q$[c]	$\phi(C_2F_4)$	$\phi(C_3HF_3)$	$\phi(C_4HF_5)$	$\phi(C_5D_8F_2)$
5.7	13.1	30.0	1.149	1.090	0.041	0.071	0.001	0.491
11.2	13.1	30.0	1.113	1.046	0.071	0.129	0.005	0.413
20.3	13.1	75.0	1.095	1.023	0.086	0.165	0.006	0.304
37.5	13.1	30.0	1.050	1.014	0.111	0.171	0.015	0.206
76.7	13.1	30.0	1.025	1.007		0.173	0.027	0.086

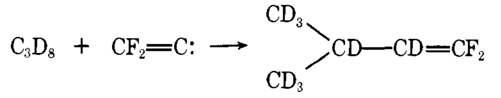
[a] I_a = 0.221 μeinstein/min, temp = 25 °C. [b] Lorentz broadening correction factor. [c] Competitive quenching correction factor calculated from $\sigma^2(C_3D_8)$ = 0.5 Å^2 and $\sigma^2(C_2HF_3)$ = 16 Å^2.

Table VII. Quantum Yields of Products from the Hg* + C_2HF_3 + C_3D_8 Reaction as a Function of Added CF_4 Pressure[a, b]

CF_4	Exposure						$\phi(CD_3CD_2CD_2CD{=}CF_2)$
Pressure, Torr	time, min	$1/f$[c]	$\phi(C_2F_4)$	$\phi(C_3HF_3)$	$\phi(C_4HF_5)$	$\phi(C_5D_8F_2)$	$\phi((CD_3)_2CDCD{=}CF_2)$
0.0	75.0	1.081	0.084	0.165	0.006	0.300	1.35
14.6	40.0	1.054	0.070		0.010	0.268	1.49
30.5	52.0	1.038	0.051	0.103	0.010	0.229	1.45
41.9	54.0	1.031	0.057		0.013	0.219	1.42
43.5	31.5	1.030	0.055	0.086	0.012	0.208	1.46
61.3	48.0	1.023	0.044	0.074	0.015	0.198	1.45
75.9	40.0	1.019	0.038		0.016	0.167	1.46
102.0	35.0	1.014	0.034	0.049	0.017	0.151	1.40
174.0	133.0	1.006	0.016	0.030	0.017	0.103	1.42

[a] I_a = 0.231 μeinstein/min, temp = 25 °C. [b] $P(C_3D_8)$ = 13 Torr and $P(C_2HF_3)$ = 20 Torr. [c] Lorentz broadening correction factor.

methyl-1-butene-d_8. The second isomer gave as the most intense peak a fragment resulting from C_2D_5 loss from the allylic position and was assigned the structure 1,1-difluoro-1-pentene-d_8. These products are the analogues of difluorovinylcyclohexane from the cyclohexane reaction and can be rationalized by the insertion reactions of difluorovinylidene into the C–D bonds of propane:



$$C_3D_8 + CF_2{=}C: \longrightarrow (CD_3)_2CD{-}CD{=}CF_2$$

$$C_3D_8 + CF_2{=}C: \longrightarrow CD_3CD_2CD_2CD{=}CF_2$$

Three series of quantitative runs were done with this system, using (a) 20 Torr C_2HF_3 and varying pressures of C_3D_8, (b) 13 Torr C_3D_8 and varying pressures of C_2HF_3, and (c) a mixture of 13 Torr C_3D_8 and 20 Torr C_2HF_3 and varying pressures of added CF_4. The results are given in Tables V–VII and shown graphically in Figures 3–5. It is seen that the scavenging reaction with propane competes efficiently with the scavenging reactions of the substrate, and propane also functions as an inert gas in deactivating the excited C_2HF_3 molecules. The ratio of the combined yield of the insertion products, $C_5D_8F_2$, to the combined yield of the addition products, C_3HF_3 (or 2 × C_2F_4) and C_4HF_5, when plotted in Figure 6 against the pressure ratio, $P(C_3D_8)/P(C_2HF_3)$, gives a straight line as required by the kinetic equation

$$\phi(C_5D_8F_2)/\phi(2 \times C_2F_4 + C_4HF_5) = \left(\frac{k_{\text{insertion}}}{k_{\text{addition}}}\right)\left(\frac{P(C_3D_8)}{P(C_2HF_3)}\right)$$

It is also to be noted that, at a given total pressure, the combined yield of insertion and addition products is independent of the ratio of C_3D_8 and C_2HF_3 pressures. Thus, we can conclude that, in the mercury photosensitization of pure C_2HF_3, all observed products arise from the reactions of difluorovinylidene with the substrate, and that the primary step of the reaction is a geminal elimination of HF

$$C_2HF_3 \xrightarrow{Hg^*} C_2HF_3^* \longrightarrow HF + CF_2{=}C: \qquad (1)$$

with an apparent quantum efficiency of ≥0.8 at zero pressure, vide supra. The occurrence of the alternative primary step

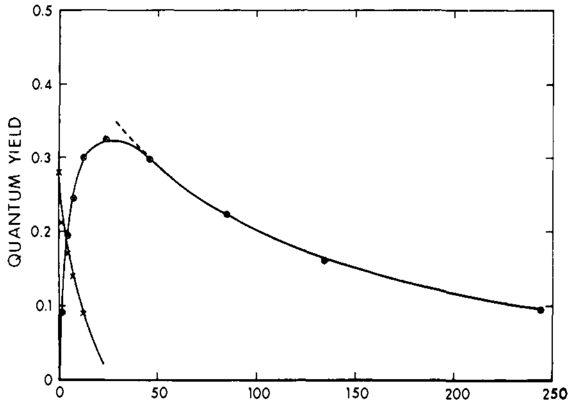


Figure 3. Quantum yields of $C_5D_8F_2$, ⊗, and C_2F_4, ×, as a function of C_3D_8 pressure at a fixed pressure of 20 Torr of C_2HF_3.

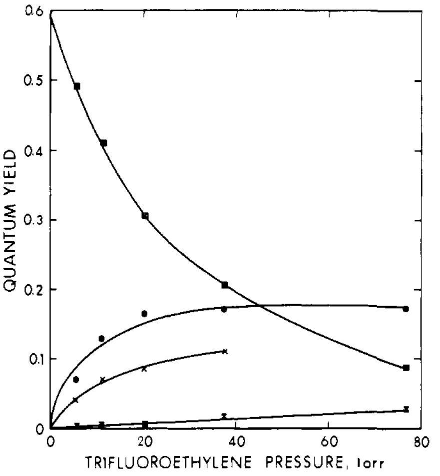


Figure 4. Quantum yields of $C_5D_8F_2$, ⊠, C_3HF_3, ⊗, C_2F_4, ×, and C_4HF_5, ⧖, as a function of C_2HF_3 pressure at a fixed pressure of 13 Torr of C_3D_8.

$$C_2HF_3 \xrightarrow{Hg^*} C_2HF_3^* \longrightarrow :CF_2 + :CFH \qquad (2)$$

to a minor extent is inferred from the mass spectrometric evidence for the presence of a small quantity of a $C_3H_2F_4$ compound in the C_4HF_5 product, which probably arises from :CFH addition to the substrate

$$C_2HF_3 + :CHF \rightarrow C_3H_2F_4 \qquad (3)$$

The yield of the $C_3H_2F_4$ products, however, is not sufficient to account for the low yield of reaction 1, and some additional primary step must be operative. Small yields of difluoroacetylene could have escaped detection and may be the source of the polymer observed in high-conversion runs.

It will also be noted from Figure 2 that, although the inert gas CF_4 effectively suppresses decomposition of the excited substrate, it has no effect on the relative rates of product formation except for collisional stabilization of C_4HF_5. The relative rate of insertion into the *primary* and *secondary* C-D bonds of propane is 1.44, and the relative rate of insertion into propane to addition to the substrate (Figure 6) is 2.53 and independent of CF_4 pressure.

The facility of the difluorovinylidene carbene insertion into C-H and C-D bonds indicates that it is formed in a singlet state. Singlet carbenes in general are known to be unreactive with molecular oxygen, but triplet carbenes react readily to yield oxidation products. To test if the reactivity of $:CF_2{=}C$ would follow a similar pattern, the mercury sensitization of C_2HF_3 was repeated in the presence of

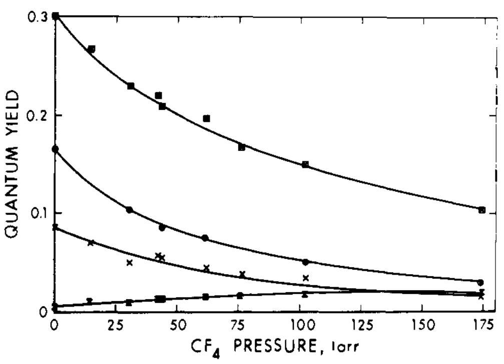


Figure 5. Quantum yields of $C_5D_8F_2$, ⊠, C_3HF_3, ⊗, C_2F_4, ×, and C_4HF_5, ⧖, as a function of added CF_4 at 13 Torr C_3D_8 and 20 Torr C_2HF_3 pressure.

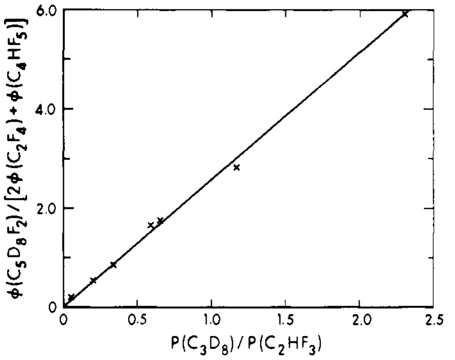


Figure 6. Variation in the quantum yield ratio $\phi(C_5D_8F_2)/[2\phi(C_2F_4) + \phi(C_4HF_5)]$ as a function of the pressure ratio $P(C_3D_8)/P(C_2HF_3)$.

added oxygen. Two new products resulted, CO_2 and CHFO, both yields rising with increasing oxygen pressure. The yields of the decomposition products (Table VIII), however, when corrected for competitive quenching of the excited mercury atoms by oxygen, are not affected. Thus, the oxidation products seem to arise from the attack of excited O_2 formed by energy transfer from Hg* upon ground-state C_2HF_3 rather than from scavenging of difluorovinylidene by ground-state O_2.

Finally, the mercury sensitization of C_2HF_3 was also investigated in the presence of added CO to determine if any of the intermediate carbenes, $:CF_2$ or $CF_2{=}C:$, could be scavenged by CO. One new product appeared in this system. It was found by high-resolution mass spectrometry to have the molecular formula C_3HF_3O which corresponds to the adduct $CO{\cdot}C_2HF_3$. The ir spectrum (Figure 1f) indicated strong bands at 1715 and 1835 cm^{-1}, suggesting the presence of two double bonds. The uv spectrum showed strong absorption at 2010 Å with a tail extending to longer wavelengths. It is tentatively identified as trifluoroacrolein. From the data summarized in Table IX, it appears that the sum of the quantum yields of C_3HF_3 and C_3HF_3O is pressure independent, indicating that C_3HF_3O forms at the expense of C_3HF_3 and in commensurate yields.

Discussion

The nature of the primary step in the triplet mercury photosensitization of C_2HF_3 has been discussed in the previous article[2] on the mercury photosensitization of mono- and difluoroethylenes. In these cases, as with olefins in general, energy transfer is believed to lead to the promotion of the molecule to its lowest (π,π^*) triplet state. When kinetically favorable, isomerization by a 1,2-hydrogen shift occurs and is then followed by decomposition: $CH_2CH_2^* \rightarrow CH_3CH:^* \rightarrow H_2 + C_2H_2$. This mechanism probably

Table VIII. Quantum Yields of Products from the Hg* + C_2HF_3 + O_2 Reaction as a Function of Oxygen Pressure[a]

Pressure, Torr		Exposure time, min	$1/f$[b]	$1/Q$[c]	$\phi(C_2F_4)$	$\phi(C_3HF_3)$	$\phi(C_4HF_5)$
C_2HF_3	O_2						
20.6		127.8	1.135	1.000	0.276	0.429	0.020
20.2	3.3	83.7	1.117	1.196	0.282	0.459	0.019
20.2	6.8	90.0	1.101	1.403	0.268	0.476	0.022
19.3	10.0	106.0	1.092	1.620	0.277	0.440	0.023

[a] I_a = 0.355 μeinstein/min, temp = 25 °C. [b] Lorentz broadening correction factor. [c] Competitive quenching correction factor calculated from $\sigma^2(O_2)$ = 13.9 Å^2 and $\sigma^2(C_2HF_3)$ = 16 Å^2.

Table IX. Quantum Yields of Products from the Hg* + C_2HF_3 + CO Reaction as a Function of Carbon Monoxide Pressure[a]

Pressure, Torr		Exposure time, min	$1/f$[b]	$1/Q$[c]	$\phi(C_2F_4)$	$\phi(C_3HF_3)$	$\phi(C_4HF_5)$	$\phi(C_3HF_3O)$
C_2HF_3	CO							
20.6	3.21	91.4	1.116	1.082	0.231	0.416	0.019	0.019
19.0	7.58	84.8	1.103	1.210	0.161	0.363	0.015	0.051
19.9	15.90	92.0	1.074	1.421	0.100	0.281	0.009	0.102
19.9	26.67	26.7	1.055	1.705	0.094	0.223	0.010	0.195

[a] I_a = 0.355 μeinstein/min, temp = 25 °C. [b] Lorentz broadening correction factor. [c] Competitive quenching correction factor calculated from $\sigma^2(CO)$ = 4.1 Å^2 and $\sigma^2(C_2HF_3)$ = 16 Å^2.

applies in the cases of ethylene, vinyl chloride, vinyl fluoride, and 1,1-difluoroethylene. In the cases of 1,2-difluoroethylene and trifluoroethylene, the only ethylidene which can be formed is the 1-fluoroethylidene, $CH_2F\text{-}\ddot{C}F$ and $CHF_2\text{-}\ddot{C}F$, since fluorine atom migration does not occur.[2] By analogy with halogenated methylenes which have a singlet ground state,[2,9] the isomerization should lead to electronically excited triplet 1-fluorovinylidenes if it follows a spin allowed path.

Empirical estimates from extended Hückel molecular orbital computations of the energy levels of triplet ethylenes and ethylidenes made it possible to calculate the rate of triplet $CF_2{=}CHF$ → triplet $CF_2H\text{-}\ddot{C}F$ isomerization. The value of the unimolecular rate constant derived[2] was 1.2 × 10^6 s^{-1}. From the present study it is possible to deduce the value of the overall decomposition rate constant and compare it to the calculated one, mentioned above.

Considering the overall mechanism as being comprised of the elementary steps

$$C_2HF_3^*\ (\text{triplet}) \rightarrow CF_2{=}C{:} + HF \qquad (1)$$

$$C_2HF_3^* + M \rightarrow C_2HF_3 + M \qquad (4)$$

followed by

$$C_2HF_3 + CF_2{=}C{:} \rightarrow C_4HF_5^* \qquad (5)$$

$$C_4HF_5^* + M \rightarrow C_4HF_5 + M \qquad (6)$$

$$C_4HF_5^* \rightarrow C_3HF_3 + {:}CF_2 \qquad (7)$$

$$2{:}CF_2 \rightarrow C_2F_4 \qquad (8)$$

the usual steady state approximation yields

$$[\phi(C_3HF_3) + \phi(C_4HF_5)]^{-1} = [2\phi(C_2F_4) + \phi(C_4HF_5)]^{-1} = \phi(1)_0^{-1} + \frac{k_4}{k_1}[C_2HF_3] \qquad (I)$$

and

$$\phi(C_4HF_5)/\phi(C_3HF_3) = \frac{k_6}{k_7}[C_2HF_3] \qquad (II)$$

where $\phi(1)_0$ is the quantum yield of reaction 1 at zero pressure. Plots of the lhs of equations I and II against pressure (Figure 7) give straight lines from which, assuming k_4 and k_6 to be equal to the gas kinetic collision frequency, 6 × 10^{10} l. mol^{-1} s^{-1}, k_1 = 1.7 × 10^8 s^{-1}, k_7 = 1.3 × 10^9 s^{-1} and $\phi(1) \geq 0.8$. Thus, the lower limit for the triplet ethylene → triplet ethylidene isomerization rate constant is 1.7 × 10^8 s^{-1}. This value is more than two orders of magnitude higher than the calculated one and hence it is unlikely that an ethylidene structure is implicated in the decomposition sequence. Instead, it would appear that decomposition occurs from the vibrationally excited triplet ethylene concertedly with intersystem crossing to ground-state decomposition products, HF + $CF_2{=}C{:}$. This is also in line with the geminal-type loss of HF, resulting in vinylidene carbene formation; geminal HF elimination can be more readily envisaged from the ethylene structure than vicinal elimination of HF from the ethylidene structure.

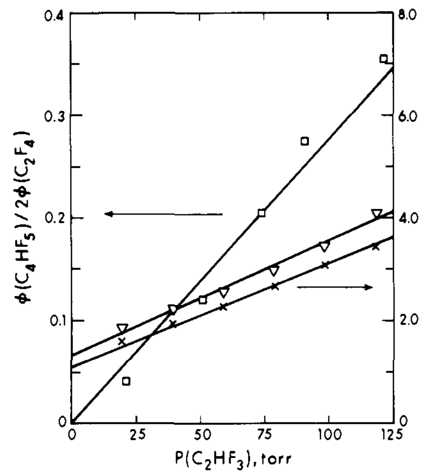


Figure 7. Plots of eq 1 and 2 vs. C_2HF_3 pressure. $A = 2\phi(C_2F_4) + \phi(C_4HF_5)$; $B = \phi(C_3HF_3) + \phi(C_4HF_5)$.

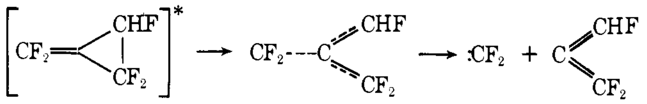
The lower than unit quantum efficiency of $CF_2{=}C{:}$ formation at zero pressure is probably due to the occurrence of other parallel primary steps such as

$$C_2HF_3^* \rightarrow {:}CF_2 + {:}CFH \qquad \Delta H \approx 82\ \text{kcal/mol}^{10} \qquad (9)$$

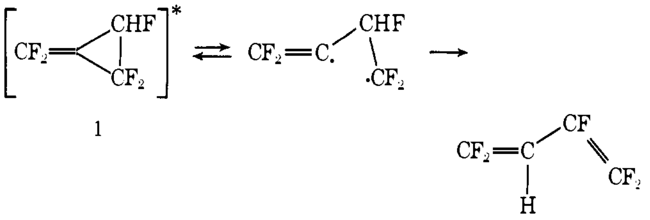
$$C_2HF_3 \rightarrow HF + CF{\equiv}CF \qquad \Delta H \approx 38\ \text{kcal/mol}^{2} \qquad (10)$$

both of which are energetically feasible. Reaction 9 is similar to the primary step in the triplet mercury photosensitized decomposition of tetrafluoroethylene in which two ground-state singlet difluoromethylenes are formed. The presence of small quantities of a $C_3H_2F_4$ compound in the trifluoroallene product is indicative of the occurrence of step 9. Difluoroacetylene formed in step 10 is highly reactive and could have escaped detection.

The addition reaction of $CF_2{=}C$: to the double bond of C_2HF_3 (step 5) affords energy-rich difluoromethylene-trifluorocyclopropane which, at the pressures employed, could not be stabilized. Stabilization could, however, be achieved with larger olefin molecules, such as tetramethylethylene.[11] The unstabilized adduct may undergo unimolecular fragmentation at a rate constant of 1.3×10^9 s^{-1} with loss of $:CF_2$ and the formation of trifluoroallene. The reaction probably proceeds in a concerted manner, rather than stepwise via a cyclopropylidene



Partial removal of the excess energy retards decomposition, but rearrangement to 1,1,2,4,4-pentafluorobutadiene still occurs



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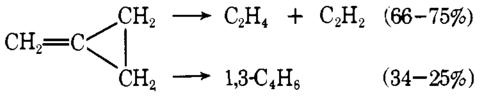
It appears that ring opening occurs exclusively between the olefinic and CF_2 carbons giving only one isomer of pentafluorobutadiene.

The addition of methylene to allene is an analogous reaction and has been reported in the literature.[12] In this system the initially formed hot methylenecyclopropane decomposes by two main routes



The former reaction was considered to proceed by flow of energy from the incipient bonds into the vinylic C-H bonds to provide the activation energy for hydrogen migration to the adjacent carbon, followed by fragmentation into acetylene and ethylene. The relative rates of these reactions remained invariant with the energy content of methylene and this was interpreted as requiring rapid equipartitioning, within less than 10^{-10} s, among strongly coupled oscillators. For **1** this mode of decomposition is much less inviting because fluorine migration requires a substantially higher activation energy than hydrogen migration and also because of the existence of an alternative low-energy path provided in reaction 7. The feasibility of this step is related to the high stability of $:CF_2$. A decomposition analogous to reaction 7 is the loss of CO from the vibrationally excited adduct of :CCO and ethylene.[13] From an energetic point of view, both CO and $:CF_2$ are good leaving groups.

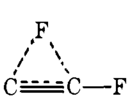
In numerous cases, allene has been postulated as the most likely rearrangement product of cyclopropylidene carbenes.[14,15]

The rearrangement reaction to 1,3-butadiene is entirely analogous to that observed in the case of methylene cyclopropane. It must involve two steps; first, removal of sufficient excess energy to prevent fragmentation and then rearrangement of the partially deactivated adduct.

The difluoromethylene formed in reaction 7 does not react with C_2HF_3 and undergoes recombination to give C_2F_4.

The insertion reaction of difluorovinylidene with paraffins provides unambiguous evidence that this species is formed in the primary step in a singlet state. Furthermore, the fact that the inert gas CF_4 has the same suppressing effect on the primary decomposition as C_2HF_3 or C_3D_8 but leaves the relative product yields unaltered, implies that $CF_2{=}C$: is formed in its ground electronic state, and that this is a singlet state. This is to be expected, since CF_2 and even monohalogenated methylenes are known to have singlet ground states,[9] and recent MO calculations predict singlet ground states for monohalogenated ethylidenes and all vinylidenes.[2]

Ab initio type molecular orbital calculations[16] on difluorovinylidene, difluoroacetylene, and the bridged structure



presumed to be the transition state for their interconversion, predict that the acetylene structure is 36.4 kcal/mol more stable than the vinylidene structure, and that fluorine migration has a prohibitively large activation energy. Similar calculations on vinylidene and acetylene indicate that the difference in the enthalpy contents of these species is 37.9 kcal/mol and that the activation energy for their interconversion is nearly half as large as that for the fluorinated analogues. These results imply that intramolecular hydrogen migration is considerably more facile and explain the lack of literature report on the detection or trapping of vinylidene.

The reactivity of difluorovinylidene is high and insertion into the C-H bonds of paraffins or addition to the double bond of C_2HF_3 probably involves a very small activation energy. This is inferred from the observed small difference in selectivity for insertion into the *secondary* vs. the *primary* C-D bonds in propane, $k(\text{C-D})_p/k(\text{C-D})_s = 0.48$ per bond and the commensurate rate of attack on C_3D_8 and C_2HF_3.

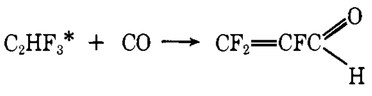
The results obtained in the reactions carried out in the presence of added oxygen (Table VIII) can be interpreted in terms of the attack of excited oxygen formed by energy transfer from Hg ($^3P_1$) atoms upon ground-state C_2HF_3 molecules

$$Hg^* + O_2 \rightarrow Hg + O_2^*$$

$$C_2HF_3 + O_2^* \rightarrow CFHO,\ CO_2,\ \text{etc.}$$

where O_2^* can be the vibrationally excited $\tilde{X}^3\Sigma_g^-$ ground state or the $\tilde{a}^1\Delta_g$, $\tilde{b}^1\Sigma_g^+$, $\tilde{C}^3\Delta_u$, $\tilde{A}^3\Sigma_u^+$, etc. excited state of the diatomic oxygen molecule. Evidently the reaction between O_2 ($\tilde{X}^3\Sigma_g^-$) and $C_2HF_3^*$, $CF_2{=}C$: or $:CF_2$ is negligibly slow under the prevailing experimental conditions.

The only new product detected in reactions with added carbon monoxide, C_3HF_3O, tentatively identified as α,β,β-trifluoroacrolein, forms at the expense of trifluoroallene and consequently is best explained in terms of the addition of CO to triplet C_2HF_3



No product attributable to the addition of carbon monoxide to any of the carbene intermediates present could be detected.

An additional report on the chemistry of difluorovinylidene will be forthcoming.

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The Strange Behavior of Lithium Salt of Tetraphenylethylene Dianion

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Abstract: We examined the optical and ^{13}C NMR spectra of the disodium and dilithium salts of tetraphenylethylene dianion (T^{2-}) as well as the spectra of their mixtures. A strong band appearing in the spectrum of $T^{2-},2Li^+$ at 385 nm is not seen in the spectrum of $T^{2-},2Na^+$. The extinction coefficient of that band is unaffected by dilution of $T^{2-},2Li^+$ even when more than 50% of the salt is dissociated into $T^{2-},Li^+ + Li^+$. In the mixture of $T^{2-},2Na^+$ and $T^{2-},2Li^+$, the relative intensity of the 385-nm band varies with the ratio Na^+/Li^+, being $\frac{1}{2}$ as intense for $Na^+/Li^+ = 1$ than for $T^{2-},2Li^+$. An appreciable upfield shift of the ethylenic ^{13}C is seen in the NMR spectrum when the hydrocarbon is reduced to its dianion, the shift being substantially greater for the dilithium than for the disodium salt. Mixture of the salts give only one NMR line for that carbon, indicating (in NMR time scale) a rapid exchange of the cations. A proposed tentative structure of these salts accounts for all the apparently inconsistent observations.

Striking differences in the optical spectra of the disodium and dilithium salts of tetraphenylethylene dianions ($T^{2-},2Na^+$ and $T^{2-},2Li^+$) were reported in our previous publication.[1] The spectrum of the disodium salt, shown in Figure 1, has a broad absorption with maximum at 485 nm ($\epsilon = 3.7 \times 10^4$). A similar absorption band appears at λ_{max} 495 nm ($\epsilon = 2.6 \times 10^4$) in the spectrum of the dilithium salt; however, as revealed by Figure 1, an additional strong peak at λ_{max} 385 nm ($\epsilon = 3.0 \times 10^4$) is seen in the spectrum of the latter salt.

The 385-nm absorption band of $T^{2-},2Li^+$ was tentatively ascribed to a charge-transfer transition;[1] however, we are exploring now an alternative explanation of this phenomenon. The intensity of the 385-nm band is clearly derived from the intensity of the 495-nm band, implying their common origin. Moreover, change of the solvent shifts both peaks, to the same degree; namely, the respective maxima are at 363 and 475 nm in dioxane, 355 and 463 nm in diethyl ether but the ratio $\epsilon_{max\ short\ wave}/\epsilon_{max\ long\ wave}$ is lower in dioxane and diethyl ether than in THF.

The present studies were initiated with the intention of gaining more information about this transition, and their results provided interesting insight into the structure of these salts. Investigation of optical spectra of analagous salts will be reported later.

NMR Studies of $T^{2-},2Na^+$ and $T^{2-},2Li^+$

The ^{13}C spectra of tetraphenylethylene (T) and of the disodium and dilithium salts of its dianion were obtained in deuterated THF by means of a Varian XL 100 NMR spectrometer equipped with a Fourier transform gear. The results are collected in Table I. The ethylenic and quaternary phenyl carbon nuclei were recognized by their long relaxation times and low intensity ($\frac{1}{4}$ and $\frac{1}{2}$, respectively, of the most abundant ortho and meta carbons), while the para carbon nuclei are again distinguished by their low intensity (equal to that of the quaternary ring carbons) but shorter relaxation time. The distinction between the most abundant meta and ortho carbons is made possible by the effect of negative charge on their position; the respective lines of the hydrocarbon and of the dianion salts virtually coincide for the meta carbons but are substantially separated for the ortho nuclei. The large upfield shift of the ethylenic line caused by the conversion of the hydrocarbon into dianion is the most striking result transpiring from the data collected in Table I. The line of the sodium salt is shifted by 43.42 ppm, and an even larger upfield shift by 52.66 ppm is observed for the lithium salt. This finding confirms the suggestion that the Li^+ cation in $T^{2-},2Li^+$ is placed closer to the dianion than the Na^+ in $T^{2-},2Na^+$. Interestingly, the