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HOT ATOM REACTIONS INVOLVING MULTIVALENT
AND UNIVALENT SPECIES

Progress Report

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II. A list of publications supported by the AEC-ERDA-DOE
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- (1) Recoil Tritium Reactions with Trimethylfluorosilane. A Study on Parameters Affecting Hot Atom Substitution Reactions, J. Phys. Chem., 75, 301-307 (1971), S.H. Daniel and Y.-N. Tang
- (2) Secondary Unimolecular Reactions Subsequent to Substitution Reactions by High-Energy Chlorine-38 and Chlorine-39 Atoms, J. Phys. Chem., 75, 440-442 (1971), Y.-N. Tang, W.S. Smith, J.L. Williams, K. Lowery, and F.S. Rowland.
- ✓ (3) Recoil Tritium Reactions with Hexamethyldisilane in the Gas Phase, J. Phys. Chem., 76, 1249-1254 (1972), S.H. Daniel, G.P. Gennaro, K.M. Ranck, and Y.-N. Tang.
- ✓ (4) Direct Evidence for the Reaction of Monomeric Silicon Difluoride with 1,3-Butadiene, J. Am. Chem. Soc., 94, 4355-4357 (1972), Y.-N. Tang, G.P. Gennaro, and Y.Y. Su.
- (5) Unimolecular Processes Subsequent to Recoil Tritium Reactions with Spiropentane, J. Phys. Chem., 76, 2187-2195 (1972), Y.Y. Su and Y.-N. Tang.
- (6) Reactions of Recoil Chlorine Atoms with cis- and trans- Olefins, J. Phys. Chem., 76, 2711-2715 (1972), W.S. Smith, S.H. Daniel, and Y.-N. Tang.
- (7) Gas Phase Recoil Phosphorus Reactions I-Complete and Partial Retention of Bonds in PF₅, J. Inorg. Nucl. Chem., 35, 3087-3094 (1973), G.P. Gennaro and Y.-N. Tang.
- (8) Addition of Singlet and Triplet Silylene to Buta-1,3-diene, J.C.S. Chem. Comm., 637-638 (1973), G.P. Gennaro, Y.Y. Su, O.F. Zeck, S.H. Daniel and Y.-N. Tang.
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- (11) The Ground Electronic State of Silylene, J. Amer. Chem. Soc., 96, 5967-5973 (1974), O.F. Zeck, Y.Y. Su, G.P. Gennaro and Y.-N. Tang.

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- (13) Interaction of Triplet Silicon Difluoride with Paramagnetic Molecules, J.C.S. Chem. Comm., 156-157 (1975), O.F. Zeck, Y.Y. Su and Y.-N. Tang.
- (14) Gas Phase Recoil Phosphorus Reactions III-Systematic Study of Hydrogen-Abstraction Reactions, J. Amer. Chem. Soc., 97, 4498-4503 (1975), O.F. Zeck, G.P. Gennaro and Y.-N. Tang.
- (15) Effect of Additives on the Reaction of Monomeric Silicon Difluoride with 1,3-Butadiene, J. Amer. Chem. Soc., 98, 3474-3477 (1976), O.F. Zeck, Y.Y. Su, G.P. Gennaro and Y.-N. Tang.
- (16) Relative Reactivities of Conjugated Dienes towards Silicon Difluoride, J.C.S. Chem. Comm., 6-7 (1977), R.A. Ferrieri, E.E. Siefert, M.J. Griffin, O.F. Zeck and Y.-N. Tang.
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- (20) Gas Phase Recoil Phosphorus Reactions IV-Effect of Moderators on Abstraction Reactions, J. Inorg. Nucl. Chem., 41, 785-789 (1979), O.F. Zeck, R.A. Ferrieri, C.A. Copp, G.P. Gennaro and Y.-N. Tang.
- (21) Reactions of Silicon Atoms and Silylenes, a chapter in "Reaction Intermediates," Volume 2, (R.A. Abramovitch, ed.), Plenum Publishing Company Limited, (total 107 pages), published in 1980, Y.-N. Tang.
- (22) Formation of 1-Silacyclopenta-2,4-diene through Recoil Silicon Atom Reactions, J. Amer. Chem. Soc., 102, 2285 (1980), E. E. Siefert, K.-L. Loh, R. A. Ferrieri, and Y.-N. Tang.

- (23) Unusual Compounds Synthesized via Nuclear Recoil Methods, a chapter in a volume of the ACS series, entitled, "Nuclear Applications in Biological, Environmental, and Pure Chemistry," (K. A. Krohn and J. W. Root, eds.), to be published in 1980, Y.-N. Tang.

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(In addition to the above, two papers have recently been submitted for publication.)

III. Progress Report for the Year, 1980-1981

A. Abstract

The major progress during this period was in the study of recoil ^{31}Si reactions. The most significant discovery is that monomeric $^{31}\text{SiF}_2$ adds to two molecules of C_2H_4 to give 1,1-difluorosilacyclopentane as a final product. In a composition study, the yield of this product rises very sharply with the addition of very small amounts of C_2H_4 , implying that C_2H_4 can capture $^{31}\text{SiF}_2$ with high efficiency. When radical scavengers were added, the yield of this product was not altered. This implies that, (i) the reacting $^{31}\text{SiF}_2$ is in its singlet ground electronic state, and (ii) the intermediate formed between $^{31}\text{SiF}_2$ and the first molecule of C_2H_4 must be molecular instead of radical in nature. When 1,3-butadiene was added to the above recoil ^{31}Si system to compete with C_2H_4 for the available $^{31}\text{SiF}_2$, a nearly complementary relationship was found between 1,1-difluorosilacyclopent-3-ene- ^{31}Si , the butadiene product, and 1,1-difluorosilacyclopentane- ^{31}Si . Quantitatively, it was deduced that butadiene is about ten times more reactive than C_2H_4 for the trapping of $^{31}\text{SiF}_2$. When Ne was added as a moderator to the 5:1 C_2H_4 :butadiene competition system, the two product ratio shifts from 1:2 in favor of butadiene to 10:1 in favor of C_2H_4 . This indicates that it is the lower energy $^{31}\text{SiF}_2$ species which is captured by C_2H_4 , while it is favorable for the more energetic $^{31}\text{SiF}_2$ to be captured by butadiene.

In the systems reacting recoil ^{31}Si atoms with C_2H_4 in the presence of PF_3 , four unidentified products with yields less than that of 1,1-difluorosilacyclopentane were also observed. Two of them were also formed when either PH_3 or $(\text{CH}_3)_3\text{P}$ were used as

the ^{31}Si precursor. This means that they are likely to be direct ^{31}Si atom reaction products. In addition, when recoil ^{31}Si atoms reacted with C_2H_4 in the presence of $(\text{CH}_3)_3\text{P}$, the main product was identified as $^{31}\text{SiH}(\text{CH}_3)_2\text{CH}=\text{CH}_2$. This might mean the formation of dimethylsilene, $^{31}\text{Si}(\text{CH}_3)_2$, and the addition of it to $\text{CH}_2=\text{CH}_2$ to give the product.

In addition, catalytic C-F hydrogenolysis of six fluoro-carbons including $\text{CH}_2=\text{CHF}$, $\text{CH}_3\text{CH}_2\text{F}$, $\text{CHF}=\text{CHF}$, $\text{CH}_2=\text{CF}_2$, CH_3CHF_2 , and CH_3CF_3 have been studied. Besides other experimental variables, the C-F hydrogenolysis at temperatures ranging from 75° to 400°C was carried out. The apparent activation energies and the A factors have been evaluated. The E_a values range from 12 kcal mol^{-1} for $\text{CH}_3\text{CH}_2\text{F}$ to 26 kcal mol^{-1} for CH_3CHF_2 and CH_3CF_3 .

B. Significant Results

During the past year (1980-1981), the main progress was in the recoil silicon- ^{31}Si reactions, centering around the new discovery that monomeric $^{31}\text{SiF}_2$ adds to ethylene to give 1,1-difluorosilacyclopentane- ^{31}Si . Some progress was also made in the studies on the interactions of molecular hydrogen and tritium on solid surfaces. The details are summarized below.

(1) Recoil ^{31}Si Reactions with C_2H_4 in the Presence of PF_3

(a) Product Spectrum. Recoil ^{31}Si atoms were formed via the nuclear transmutation, $^{31}\text{P}(\text{n},\text{p})^{31}\text{Si}$, initiated by fast neutrons either from a nuclear reactor or from a cyclotron source with a 16-MeV deuteron beam impinging on a beryllium target. In these systems, PF_3 served both as the source of P atoms for the nuclear reaction and as the source of F atoms for the abstraction by ^{31}Si atoms to form $^{31}\text{SiF}_2$. The product spectrum of recoil ^{31}Si reactions with C_2H_4 in the presence of PF_3 (30% C_2H_4 , 70% PF_3) is displayed in Figure 1 in which a 20 ft Silicon Oil column at 25°C was used for analysis. Columns of very long retention times were employed to guarantee adequate separation of the reaction products. The major product with a retention time of 195 min was identified with the calibration of authentic samples as 1,1-difluorosilacyclopentane- ^{31}Si (DFSCPA*). This identification was confirmed on three other columns with different separation characteristics: (i) a 17 ft Dimethylsulfolane column (DMS) at 25°C; (ii) a 30 ft Silicon Fluid-96 column (SF96) at 40°C; and (iii) a combined column of 10 ft Silicon Oil and 10 ft SF96

Figure 1. Product spectrum from recoil ³¹Si reactions with C₂H₄ in the presence of PF₃, (30% C₂H₄, 70% PF₃); analyzed on a 20 ft. silicon oil column at 25°C

at 25°C. The retention times of various silicon-containing compounds on the four employed columns are listed in Table 1.

The identification of DFSCPA* as a product in this system indicates that the $^{31}\text{SiF}_2$ formed by F-abstraction can add to two molecules of C_2H_4 .

The decay-corrected yields of the five products are also shown in Figure 1. The basis for the arbitrary values of the product yields is that every 200 units is equivalent to an absolute yield of 1%. It can be seen that DFSCPA* has an absolute yield of about 10%. The four unknown products, which were labeled as A-17, B-38, C-93, and D-120, (the numerals indicate the retention times), are all smaller and shorter in retention times than that of DFSCPA*. As seen in Table 1, a large variety of Si-containing compounds have been synthesized and calibrated. However none of the products agree with the calibrated compounds in retention times on all four GC columns.

At first it was thought that product D-120 might be $^{31}\text{SiH}_2(\text{CH}=\text{CH}_2)_2$ formed by the interactions of ^{31}Si atoms with two molecules of C_2H_4 .

Since subsequent calibrations indicate that $\text{SiH}_2(\text{CH}=\text{CH}_2)_2$ has a much shorter retention time than that of D-120, another

Table 1

Retention Times of Silicon-Containing Compounds on Four Different Columns

	20 ft Silicon Oil (25°C)	10 ft Silicon Oil 10 ft SF96 (25°C)	30 ft SF96 (40°C)	17 ft DMS (25°C)
SiH_4	5	5	8	4
$\text{SiH}_3\text{CH}=\text{CH}_2$	12	7	18	6
$\text{SiH}_3\text{CH}_2\text{CH}_3$	14	8	21	7
$\text{SiH}(\text{CH}_3)_2\text{CH}=\text{CH}_2$	--	27	--	--
60	31	71	35
77	36	85	30
$\text{SiH}_3(\text{C}_4\text{H}_9)$	84	41	100	25
90	47	110	28
205	110	195	90
210	115	157	194
182	114	185	99
191	114	193	112
175	99	167	215
248	--	--	--

possible candidate for its identity could be $^{31}\text{Si}(\text{CH}_2\text{CH}_3)_2(\text{CH}=\text{CH}_2)_2$ formed by the following interaction of recoil ^{31}Si atoms.

Other compounds under consideration for future calibrations of these four unknown compounds are $\text{SiH}_3\text{C}\equiv\text{CH}$, $\text{SiHF}_2\text{CH}=\text{CH}_2$, and the silicon compounds with an unsaturated four carbon straight chain.

(b) Composition Studies. A series of studies have been carried out in which the mole % of C_2H_4 was varied from 0.5% to 90%. The results are summarized in Table 2. In Figure 2, the DFSCPA* yields were plotted as a function of the mole % of C_2H_4 . It is seen that the DFSCPA* yield rises very sharply with the addition of very small amounts of C_2H_4 , implying that C_2H_4 can capture $^{31}\text{SiF}_2$ with high efficiency. A maximum in yield is reached at about 20% C_2H_4 and then a gradual decline follows. The exhibition of a maximum confirms that DFSCPA* is indeed a cross-product of PF_3 and C_2H_4 as indicated in equations (1) and (2).

A 7 ft DMS column was used for the analysis of this composition variation series. The C-93 and D-120 products were not separated in this short column. In Figure 3, the yields of these combined peaks were plotted as a function of $\text{C}_2\text{H}_4\%$ in the samples. A nearly linear increase is observed, similar to the variation observed for the silacyclopentadiene- ^{31}Si yield in the PF_3 - 1,3-butadiene system. Such a linear dependence on $\text{C}_2\text{H}_4\%$ indicates that products C-93 and/or D-120

Table 2.

Yields of Products Derived from Recoil ^{31}Si Reactions with C_2H_4 in the Presence of PF_3
with Composition as a Variable

Sample Composition (Pressure in cm Hg)		$\text{\%C}_2\text{H}_4$	Product Yields			
P_{PF_3}	$\text{P}_{\text{C}_2\text{H}_4}$		A-17	B-38	C-93, D-120
91	0.49	0.54	1330	--	33	223
87	0.88	1.00	1377	--	61	558
89	1.66	1.83	1506	--	128	826
87	4.54	4.96	1311	--	439	1553
83	9.76	10.50	1500	--	650	2317
75	17	19	1212	--	883	2772
73	18	20	1080	--	727	2602
65	27	30	1100	--	1115	2092
61	31	33	1546	--	956	2116
47	46	50	1240	241	2292	2119
40	52	57	1238	95	1908	2306
39	52	57	1058	127	1996	2602
32	61	65	1579	nm	nm	2003
25	57	73	1093	366	2208	1669

Table 2 (cont.)

Sample Composition (Pressure in cm Hg)		C_2H_4	Product Yields			
P_{PF_3}	$\text{P}_{\text{C}_2\text{H}_4}$		A-17	B-38	C-93, D-120	SiF_2
23	68	75	1127	247	2307	2021
15	80	86	nm	nm	3164	1439
9.28	85	90	1136	216	2504	1010
4.64	86	95	1257	327	2449	nm

Figure 2. Variation of DFSCPA* yield as a function of mole % of C_2H_4 in the $PF_3-C_2H_4$ mixture. $\bigcirc$, DFSCPA*.

Figure 3. Variation of the yields of other products as a function of mole % of C_2H_4 in the $PF_3-C_2H_4$ mixture. $\circ$, peak A-17; $\triangle$, peak B-38; $\square$, peak C-93.

are formed without the involvement with PF_3 molecules as a precursor. In other words, they are likely to be products resultant from ^{31}Si atoms instead of $^{31}\text{SiF}_2$ reactions. This is the reason why reactions (3) and (4) are suspected to be involved in their formation.

The variation of the other two unknown products, A-17 and B-38, with $\text{C}_2\text{H}_4\%$ are also shown in Figure 3. The former decreases while the latter increases slightly with the addition of C_2H_4 .

(c) Scavenger Effect. The effect of scavengers such as NO and O_2 on the product yields from recoil ^{31}Si reactions in the $\text{PF}_3 - \text{C}_2\text{H}_4$ systems have been studied. The effect is graphically illustrated in Figure 4 with chromatograms, and the results are summarized in Tables 3 - 5. In Table 3, the results are obtained from a series of samples with a constant $\text{PF}_3/\text{C}_2\text{H}_4$ ratio but with varying amounts of NO . As the plotting in Figure 5 indicates, the DFSCPA* yield is essentially unchanged with the addition of up to 10% NO . In contrast, the yields of both C-93 and D-120 decrease extremely sharply with the addition of as little as 0.5% of NO . In Tables 4 and 5, constant amounts of NO and O_2 , respectively, are used in $\text{PF}_3 - \text{C}_2\text{H}_4$ samples where the mole % of C_2H_4 changes. The values of the DFSCPA* yields from these two Tables as a function of $\text{C}_2\text{H}_4\%$ are plotted in Figure 6 for such NO - or O_2 -scavenged samples. When the observed variation is compared with that in Figure 3, it is concluded that the addition of a scavenger does not affect the DFSCPA* yield throughout the whole composition range. This implies that, (i) the reacting $^{31}\text{SiF}_2$ in equation

Figure 4. Gas chromatogram illustrating the effect of NO on the yields of products derived from recoil ^{31}Si reactions with C_2H_4 in the presence of PF_3 .

Table 3

Effect of NO on the Yields of Products Derived from Recoil ^{31}Si Reactions
with a Constant Mixture of PF_3 and C_2H_4

Sample Composition (Pressure in cm Hg)			%NO	Product Yields				
P_{PF_3}	$P_{\text{C}_2\text{H}_4}$	P_{NO}		A-17	B-38	C-93,	D-120
62	31	none	0	808	194	1959		2359
66	27	0.18	0.19	1125	33	182	38	2278
63	31	0.60	0.64	1260	---	152		2405
64	27	0.94	1.02	1219	75	105	38	2110
55	31	4.00	4.45	1213	---	75		2514
60	27	4.62	5.05	1722	130	182	0	2555
52	32	9.26	9.95	1218	---	283		2544

Table 4

Yields of Products Derived from Recoil ^{31}Si Reactions with $\text{PF}_3\text{-C}_2\text{H}_4$ Mixtures
in the Presence of NO

Sample Composition (Pressure in cm Hg)			$\text{\%C}_2\text{H}_4$	Product Yields		
P_{PF_3}	$P_{\text{C}_2\text{H}_4}$	P_{NO}		A-17	C-93, D-120
88	0.9	4.5	1.0	96	4.0	868
86	1.9	4.5	2.1	185	2.4	1767
82	4.6	4.5	5.1	452	21	3113
77	9.1	4.4	10.0	562	22	2782
68	18	4.5	20	972	55	2852
36	50	4.6	55	2455	154	2356
14	72	4.5	80	3116	246	1238
4.4	81	4.5	90	2992	---	857

Table 5
 Yields of Products Derived from Recoil ^{31}Si Reactions with $\text{PF}_3\text{-C}_2\text{H}_4$ Mixtures
 in the Presence of O_2

Sample Composition (Pressure in cm Hg)			C_2H_4	Product Yields		
P_{PF_3}	$\text{P}_{\text{C}_2\text{H}_4}$	P_{O_2}		A-17	C-93, D-120
78	9.2	4.5	10.1	255	267	1602
58	27	4.6	30	732	797	2372
31	54	4.4	60	1142	1436	2509
8.5	77	4.5	85	1617	1894	nm

Figure 5. Effect of NO on the yields of products derived from recoil ^{31}Si reactions with a constant mixture of PF_3 and C_2H_4 . $\triangle$, peak A-17; $\square$, peak B-38; $\circ$, (peak C-93 + peak D-120); $\times$, DFSCPA*.

Figure 6. Variation of product yields as a function of sample composition for recoil ^{31}Si reactions with $\text{PF}_3\text{-C}_2\text{H}_4$ mixtures in the presence of NO or O_2 . $\triangle$, peak A-17 in 5% NO ; $\blacktriangle$, peak A-17 in 5% O_2 ; $\circ$, (peak C-93 + peak D-120 in 5% NO); $\bullet$, (peak C-93 + peak D-120 in 5% O_2); $\square$, DFSCPA* in 5% NO ; $\blacksquare$, DFSCPA* in 5% O_2 .

(1) is likely to be in its singlet ground electronic state, and (ii) whatever intermediate formed between $^{31}\text{SiF}_2$ and the first molecule of C_2H_4 must be molecular instead of radical in nature. A plausible mechanism involves the formation and the subsequent interaction of an excited silacyclopropane intermediate.

As seen in Table 4 and Figure 6, the yields of the combined C-93 and D-120 peaks in the NO -scavenged samples are again extremely low. They are much lower than the corresponding yields of the same products in the unscavenged systems as shown in Figure 3. This implies that either triplet ^{31}Si atoms or radical intermediates must be involved in the formation of these products. However, the O_2 -scavenged samples are different in this aspect. The combined C-93 and D-120 yields are only slightly decreased from those of the unscavenged samples. The only possible explanation for these results is that O_2 is quantitatively removed in the system before or during the irradiation.

(d) Moderator Effect. The effect of Ne as a moderator on the product yields derived from recoil ^{31}Si reactions with $\text{PF}_3 - \text{C}_2\text{H}_4$ systems have been studied. The results are summarized in Table 6 and are plotted in Figure 7. Because of experimental complications, only reliable yields of DFSCPA*

Table 6

Effect of Ne on Products Derived from Recoil ^{31}Si Reactions
with a Constant Mixture of PF_3 and C_2H_4

Sample Composition (Pressure in cm Hg)			%Ne	Product Yields	
P_{PF_3}	$P_{\text{C}_2\text{H}_4}$	P_{Ne}		A-17
65	27	0	0	543	1977
47	20	26	28	833	2019
31	14	47	51	601	2143
16	6.9	68	75	504	2574
6.3	2.8	81	90	677	2429

Figure 7. Variation of product yields as a function of Ne concentration for recoil ^{31}Si reactions with $\text{PF}_3\text{-C}_2\text{H}_4$ mixtures. $\triangle$, peak A-17; $\square$, peak DFSCPA*.

and A-17 were obtained. It is seen in the plotting that the yield of DFSCPA* increases somewhat with Ne-moderation while that of A-17 remains essentially constant. The increase of the DFSCPA* yield implies that reaction (1) is a rather low energy process.

(2) Recoil ^{31}Si Reactions with C_2H_4 - 1,3-Butadiene Mixtures in the Presence of PF_3

(a) Product Variation with Mole % of 1,3-Butadiene in the Mixture. Monomeric $^{31}\text{SiF}_2$ can also be trapped efficiently by 1,3-butadiene to give 1,1-difluorosilacyclopent-3-ene- ^{31}Si , (DFSCPE*).

As butadiene is added to a $\text{PF}_3\text{-C}_2\text{H}_4$ system, reaction (7) will be in competition with reaction (1). In other words, both C_2H_4 and butadiene will be competing for the available monomeric $^{31}\text{SiF}_2$. Such a situation is demonstrated in Figure 8 with gas chromatograms of four samples ranging from pure C_2H_4 systems to pure butadiene systems. As can be seen in the illustration, as the composition of the mixture shifts in favor of butadiene, the DFSCPA* yield decreases while the DFSCPE* yield increases. Actually, in samples with 50% butadiene, the yield of DFSCPA* is already negligible.

In Table 7, the quantitative results of the competition systems are given. The yields of DFSCPA*, DFSCPE*, silacyclopentadiene- ^{31}Si , (SCPA*), and the four unidentified products from the $\text{PF}_3\text{-C}_2\text{H}_4$ systems are all listed for samples ranging

Figure 8. Gas chromatograms illustrating the competition of C_2H_4 and 1,3-butadiene for $^{31}SiF_2$.

Activity (Counts/Min)

Table 7

Yields of Products Derived from Recoil ^{31}Si Reactions with C_2H_4 -1,3-Butadiene Mixtures in the Presence of PF_3

(Analysed with 20 ft Silicon Oil Column)

Sample Composition (Pressure in cm. Hg)			%	Product Yields						
P_{PF_3}	$P_{\text{C}_2\text{H}_4}$	$P_{\text{1,3-butadiene}}$		A-17	B-38	C-93	D-120
63	27	0	0	1052	145	618	476	0	0	2070
65	27	0	0	1302	170	659	586	0	0	1977
63	26	1.4	1.6	637	59	513	207	161	490	1438
63	25	2.6	2.9	519	55	452	219	253	842	1020
65	24	2.7	2.9	488	87	435	134	173	548	972
24	23	4.4	4.8	365	45	317	90	402	959	850
65	18	8.9	9.8	499	83	236	49	695	1398	366
65	13	13	14	121	34	86	0	715	1860	64
63	8.9	18	20	173	41	55	0	1177	nm	0
63	7.2	20	23	110	19	45	0	1135	nm	0
65	0	27	30	0	0	0	0	1323	1763	0

from pure C_2H_4 to pure 1,3-butadiene. These samples were analysed with the long 20 ft Silicon Oil column where all the products were well separated and well-preserved. On the other hand, there are a number of samples which were analysed with a different Silicon Oil column where only the yields of DFSCPA* and DFSCPE* are dependable because there are carriers for them. The results of these samples are shown in Table 8. The absolute yields of DFSCPA* and DFSCPE* for all the samples in Tables 7 and 8 are plotted in Figure 9, as a function of mole % of 1,3-butadiene. In addition, the yields of SCPA* and the four unidentified products as listed in Table 7 are plotted in Figure 10 on a similar base.

The data in Figure 9 demonstrates that both DFSCPA* and DFSCPE* are derived from the same precursor. It is seen that essentially the same amount of $^{31}SiF_2$ was captured by each of the two olefins in the systems where only C_2H_4 and butadiene are present. As the mole fraction of butadiene increases, the DFSCPA* yield decreases sharply while a corresponding increase in the DFSCPE* yield is observed. The two yields are nearly complementary to each other. Quantitatively, if the two yields were totaled and plotted against the mole fractions of the olefins, a shallow minimum amounting to about 15% depression results at the composition where the two products exhibit similar yields. The missing portion is probably due to the formation of a presently undetected ethylene-butadiene cross-product, resultant from the interaction of an initial $^{31}SiF_2 - C_2H_4$ adduct with a molecule

Table 8

Yields of DFSCPA* and DFSCPE* from Recoil ^{31}Si Reactions
 with C_2H_4 -1,3-Butadiene Mixtures in the Presence of PF_3
 (Analysed with a Silicon Oil Column which is not well-conditioned)

Sample Composition (Pressure in cm Hg.)			%	Product Yields	
P_{PF_3}	$P_{\text{C}_2\text{H}_4}$	$P_{\text{1,3-butadiene}}$
63	27	0	0	0	2100
62	31	0	0	0	1896
64	27	0	0	0	1980
64	27	0	0	0	1959
61	31	0	0	0	2116
65	27	0	0	0	2092
66	27	0	0	0	1864
66	26	1.2	1.3	427	1453
63	25	1.9	2.1	570	1089
65	25	2.0	2.2	761	1105
63	24	3.1	3.4	918	790
63	23	4.6	5.1	1214	546
65	23	4.9	5.3	1350	683
63	20	6.8	7.6	1600	264
66	18	9.2	9.9	1895	240
64	14	12	14	2015	47
63	14	13	15	1724	182
65	8.1	19	21	2140	9.1
66	0	27	29	2072	0
65	0	27	30	1984	0

Table 8 (con't.)

Sample Composition (Pressure in cm. Hg)				Product Yields	
P_{PF_3}	$P_{C_2H_4}$	P_{diene}
63	0	27	30	2015	0
62	0	27	31	1867	0
62	0	28	31	2120	0
62	0	30	33	2000	0

Figure 9. Variation of the absolute yields of DFSCPA* and DFSCPE* with the mole % of 1,3-butadiene in recoil ^{31}Si systems with C_2H_4 -butadiene- PF_3 mixtures. $\square$, DFSCPE*; $\circ$, DFSCPA*.

Figure 10. Variation of the yields of SCPA* and other products with the mole % of 1,3-butadiene in recoil ^{31}Si systems with C_2H_4 -butadiene- PF_3 mixtures. $\triangle$, SCPA*; $\times$, peak A-17; $\oplus$, peak B-38; $\circ$, peak C-93; $\square$, peak D-120.

of butadiene. Besides the demonstration of complementarity, these results also provide information about the relative reactivities of the two olefins. In the figure, the olefinic composition where the DFSCPA* and the DFSCPE* yields are identical corresponds to 3% butadiene and 27% C_2H_4 . Such an observation implies that butadiene is about ten times more reactive than ethylene for the trapping of $^{31}SiF_2$.

Figure 10 illustrates that as the mole % of 1,3-butadiene increases, the yield of SCPA* increases linearly. This is in accord with the mode of formation for SCPA* from the direct combination of ^{31}Si atoms with butadiene.

On the other hand, the four unidentified products derived from the interaction of recoil ^{31}Si atoms with C_2H_4 decrease sharply with the addition of butadiene. In particular, the decrease in the yield of D-120 is extremely sharp. With the addition of a mere 2% of butadiene, the yield of D-120 decreases by about two-thirds. Such a decrease agrees with the earlier assessment from the scavenger results, that a radical intermediate is likely to be involved in its formation because butadiene can also act as an efficient scavenger for radicals. This also means that reaction (4) is a possible means for its formation because radical intermediates must be involved for the formation of $^{31}Si(CH_2CH_3)_2(CH=CH_2)_2$ from the interaction of ^{31}Si with four molecules of C_2H_4 .

(b) Scavenger Effect for the Mixture System. Table 9 summarizes the results of the C_2H_4 -butadiene competition systems when a constant amount of 5% NO was added. Again, only the yields of DFSCPA* and DFSCPE* are given because the yields of all other products are not reliable due to poor column conditions. The yields of these two observed products are plotted in Figure 11. It is seen that the DFSCPA* yield decreases with mole % of butadiene in a fashion which is quantitatively similar to what is shown in Figure 9. This means that NO has no effect on reaction (2) even in the presence of various amounts of butadiene. On the other hand, the DFSCPE* yield in Figure 11 increases much more steeply with mole % of butadiene than what has been observed in Figure 9. In fact, at 30% butadiene, the yield of DFSCPE* is more than twice as high in the presence of NO in comparison with the situation when NO is absent. This is again in accord with the previously published results that the addition of NO increases the yield of DFSCPE* in the $^{31}SiF_2$ -butadiene system. The increase was attributed to the capture of triplet $^{31}SiF_2$ through complex formation with NO, and then the $^{31}SiF_2$ -NO complex acted as a $^{31}SiF_2$ -donor towards butadiene.

(c) Moderator Effect for the Mixture Systems. The addition of Ne as a moderator will decrease the average translational energy of the reacting species such as ^{31}Si atoms and $^{31}SiF_2$. Experiments have been performed where varying amounts of Ne were added to a $^{31}SiF_2$ system with a constant C_2H_4 to butadiene ratio of 5:1. The observed yields of products are summarized in Table 10. Without the moderator, the DFSCPA* to DFSCPE*

Table 9

Yields of DFSCPA* and DFSCPE* from Recoil ^{31}Si Reactions
with C_2H_4 -1,3-Butadiene- PF_3 Mixtures in the Presence of NO

Sample Composition (Pressure in cm Hg)				%	Product Yields	
P_{PF_3}	$P_{\text{C}_2\text{H}_4}$	P_{NO}	$P_{\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2}$		$^{31}\text{SiF}_2$	$^{31}\text{SiF}_2$
60	27	4.6	0	0	0	2555
59	28	4.1	0	0	0	1923
61	27	4.5	0	0	0	2037
58	23	4.6	4.4	4.9	1785	695
59	23	4.6	4.4	4.9	1546	588
59	14	4.5	13	15	2384	106
58	14	4.5	14	15	3009	118
60	0	4.6	27	30	4455	0
59	0	4.8	27	30	4412	0
59	0	4.5	27	30	4367	0
59	0	4.6	27	30	4460	0

Figure 11. Variation of the yields of DFSCPA* and DFSCPE* with the mole % of 1,3-butadiene in recoil ^{31}Si systems with C_2H_4 -butadiene- PF_3 mixtures in the presence of NO . $\square$, DFSCPA*; $\triangle$, DFSCPE*.

Table 10

Effect of Ne on Recoil ^{31}Si Reactions with 5:1 C_2H_4 :1,3-Butadiene Mixtures
in the Presence of PF_3

Sample Composition (Pressure in cm. Hg)				%Ne	Product Yields					
P_{PF_3}	$P_{\text{C}_2\text{H}_4}$	$P_{\text{CH}_2=\text{CH}=\text{CH}=\text{CH}_2}$	P_{Ne}		A-17	C-93	D-120	$^{31}\text{SiH}_2$	$^{31}\text{SiF}_2$	$^{31}\text{SiF}_2$
63	23	4.6	0	0	557	nm	nm	nm	1535	690
65	23	4.9	0	0	448	nm	nm	nm	1350	683
47	17	3.7	23	25	nm	nm	nm	nm	1413	703
39	14	2.9	35	38	467	nm	nm	nm	1127	687
32	11	2.4	45	50	546	nm	nm	nm	1214	697
32	11	2.3	45	50	654	538	57	756	1312	1005
24	9.5	1.7	57	63	nm	nm	nm	nm	1482	962
16	5.7	1.1	67	75	647	563	90	734	1194	1230
17	5.6	1.2	68	75	622	nm	nm	nm	1314	1177
11	3.9	0.8	75	83	747	nm	nm	nm	1303	1429
6.3	2.3	0.5	81	90	795	740	147	565	950	2153
6.2	2.2	0.6	83	90	756	nm	nm	nm	720	2139
3.2	1.1	0.2	86	95	857	nm	nm	nm	341	2922

product ratio is about 1:2. As shown in Figure 12, the yield of the former increases while that of the latter decreases with Ne-moderation. With the addition of 95% Ne, the DFSCPA* to DFSCPE* ratio shifts to about 10:1. This indicates that it is the lower energy $^{31}\text{SiF}_2$ species which is captured by C_2H_4 , while it is favorable for the more energetic $^{31}\text{SiF}_2$ to be captured by butadiene. As seen in Table 10, the yields of the other products in this mixture system are less sensitive to Ne-moderation. Most of them show a gradual increase with the addition of Ne.

Parallel Ne-moderation studies with constant C_2H_4 to butadiene ratios of 14:1 and 1:1 have also been carried out. The results are listed in Tables 11 and 12, and plotted in Figures 13 and 14, respectively. A similar conclusion that can also be drawn is that the DFSCPA* yield increases while the DFSCPE* yield decreases with Ne-moderation. Therefore, reaction (2) is always a lower energy process than reaction (7) regardless of the sample composition.

Some preliminary studies have also been initiated using He and Xe as moderators in the recoil ^{31}Si reactions with C_2H_4 -butadiene- PF_3 mixtures.

(3) Recoil ^{31}Si Reactions with C_2H_4 in the Presence of PH_3

Recoil ^{31}Si reactions with C_2H_4 in the presence of PH_3 have been carried out. The most surprising result is that silacyclopentane- ^{31}Si is not a product of this system as was expected from the formation of DFSCPA* from the parallel reaction of $^{31}\text{SiF}_2$ with C_2H_4 . The absence of silacyclopentane- ^{31}Si

Figure 12. Variation of the yields of DFSCPA* and DFSCPE* with the mole % of Ne in recoil ^{31}Si reactions with 5:1 C_2H_4 :1,3-butadiene mixtures in the presence of PF_3 . $\square$, DFSCPA*; $\triangle$, DFSCPE*.

Table 11

Effect of Ne on Recoil ^{31}Si Reactions with 14:1 C_2H_4 :1,3-Butadiene Mixtures
in the Presence of PF_3

Sample Composition (Pressure in cm Hg)				%Ne	Product Yields		
P_{PF_3}	$P_{\text{C}_2\text{H}_4}$	$P_{\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2}$	P_{Ne}		A-17	$^{31}\text{SiF}_2$	$^{31}\text{SiF}_2$
63	25	1.9	0	0	530	570	1089
32	13	0.9	45	50	528	491	1073
16	6.4	0.4	68	75	762	590	1335
6.3	2.6	0.2	82	90	649	278	2383
3.2	1.3	0.1	86	95	530	220	2955

Table 12

Effect of Ne on Recoil ^{31}Si Reactions with 1:1 C_2H_4 :1,3-Butadiene Mixtures
in the Presence of PF_3

Sample Composition (Pressure in cm Hg)				%Ne	Product Yields					
P_{PF_3}	$P_{\text{C}_2\text{H}_4}$	$P_{\text{1,3-butadiene}}$	P_{Ne}		A-17	C-93	D-120	$^{31}\text{SiH}_2$	$^{31}\text{SiF}_2$	$^{31}\text{SiF}_2$
64	13	13	0	0	121	nm	nm	715	1860	64
31	6.8	6.8	45	50	333	nm	nm	nm	1608	97
32	6.9	6.7	45	50	296	131	nm	1463	1721	242
16	3.5	3.2	68	75	281	nm	nm	nm	1459	314
6.4	1.4	1.3	82	90	533	194	nm	1657	nm	527
6.3	1.3	1.4	83	90	303	nm	nm	nm	1256	506
3.6	0.9	0.5	87	95	388	nm	nm	nm	892	1491

Figure 13. Variation of the yields of DFSCPA* and DFSCPE* with the mole % of Ne in recoil ^{31}Si reactions with 14:1 C_2H_4 :1,3-butadiene mixtures in the presence of $^2\text{PF}_3$. $\square$, DFSCPA*; $\triangle$, DFSCPE*.

Figure 14. Variation of the yields of DFSCPA* and DFSCPE* with the mole % of Ne in recoil ^{31}Si reactions with 1:1 C_2H_4 :1,3-butadiene mixtures in the presence of PF_3 . $\square$, DFSCPA*; $\triangle$, DFSCPE*.

as a product means that in the presence of PH_3 , $^{31}\text{SiH}_2$ does not undergo the following process.

The product spectrum from recoil ^{31}Si reactions with the $\text{PH}_3\text{-C}_2\text{H}_4$ system is shown at the bottom part of Figure 15. This sample is analysed with the combined column of 10 ft Silicon Oil and 10 ft SF96. Six ^{31}Si -labeled products are observed with the last two emerging at similar retention times to the C-93 and D-120 peaks of the $\text{PF}_3\text{-C}_2\text{H}_4$ system. In order to demonstrate that they are indeed the same products, two samples, one of $\text{PF}_3 + \text{C}_2\text{H}_4$, another of $\text{PH}_3 + \text{C}_2\text{H}_4$, were premixed and then analysed on the above-mentioned combined column. The chromatogram is shown in the middle of Figure 15. Since single peaks were obtained from such mixed samples, it is concluded that the same products, C-93 and D-120, are produced from the reactions of recoil ^{31}Si with both the $\text{PF}_3\text{-C}_2\text{H}_4$ and the $\text{PH}_3\text{-C}_2\text{H}_4$ systems. This information implies that both C-93 and D-120 are ^{31}Si atom reaction products instead of derived from either $^{31}\text{SiF}_2$ or $^{31}\text{SiH}_2$.

(4) Trimethyl Phosphine as a Source of Recoil ^{31}Si Atoms

In addition to PH_3 and PF_3 , recent experiments have employed $(\text{CH}_3)_3\text{P}$ as an alternative recoil ^{31}Si source. The chromatogram of a pure $(\text{CH}_3)_3\text{P}$ system is shown on the top of Figure 16. When C_2H_4 was added to the $(\text{CH}_3)_3\text{P}$ system for recoil ^{31}Si reactions, several additional products were observed, as illustrated at the bottom of Figure 16. A very noticeable

Figure 15. Gas chromatogram demonstrating the formation of common ^{31}Si -labeled products from the $\text{PF}_3 + \text{C}_2\text{H}_4$ and $\text{PH}_3 + \text{C}_2\text{H}_4$ systems.

Figure 16. Gas chromatogram showing the formation of $\text{SiH}(\text{CH}_3)_2\text{CH}=\text{CH}_2$ from recoil ^{31}Si reactions with $(\text{CH}_3)_3\text{P}-\text{C}_2\text{H}_4$ mixed system.

Activity (Counts/Min)

product is the major product of the system which is tentatively identified as $\text{SiH}(\text{CH}_3)_2\text{CH}=\text{CH}_2$. If this is confirmed, the following sequence of reactions may be responsible for its formation.

This means that dimethylsilylene- ^{31}Si , $^{31}\text{Si}(\text{CH}_3)_2$, may have been involved as an intermediate in this system.

(5) Systematic Studies of the O_2 -Effect on Recoil ^{31}Si Reactions with 1,3-Butadiene in the Presence of PF_3

In order to continue the study on recoil ^{31}Si reactions with 1,3-butadiene in the presence of PF_3 , a systematic study of the O_2 -effect on this system has been performed. In Figure 17, the effect of O_2 on the formation of DFSCPE* from $^{31}\text{SiF}_2$ with butadiene is shown. Four series of samples with different O_2 levels have been studied: 0, 1, 5, and 20% O_2 . The general shape of the trends are similar to what has been obtained earlier when various amounts of NO were added to similar series. The difference is that in the case of NO, quantitatively every series reaches a similar specific yield as a maximum regardless of the amount of NO added. In the case of O_2 , as seen in Figure 17, the maximum values of each series decreases as the amount of O_2 added to each series increases.

In Figure 18, the effect of various amounts of O_2 on the formation of SCPA* from reaction (8) is shown. It is obvious that O_2 essentially has no effect on the quantitative yields of SCPA*.

Figure 17. Dependence of DFSCPE* yield on the composition of PF_3 -1,3-butadiene mixtures in the presence of various amounts of O_2 . +, DFSCPE* in pure samples; $\triangle$, DFSCPE*² in 1% O_2 ; $\square$, DFSCPE* in 4% O_2 ; $\circ$, DFSCPE* in 20% O_2 .

Figure 18. Dependence of SCPA* yield on the composition of PF₃-1,3-butadiene mixtures in the presence of various amounts of O₂. $\square$, SCPA* in pure samples; $+$, SCPA* in 1% O₂; $\triangle$, SCPA* in 4% O₂; $\circ$, SCPA* in 20% O₂.

(6) Catalytic Hydrogenolysis of Fluorocarbons on Pd Surfaces

A paper entitled "Heterogeneous Hydrogenolysis of some Fluorocarbons" has very recently been submitted for publication. A preprint of this article is included with the report. In this work, the catalytic C-F hydrogenolysis of six fluorocarbons including $\text{CH}_2=\text{CHF}$, $\text{CH}_3\text{CH}_2\text{F}$, $\text{CHF}=\text{CHF}$, $\text{CH}_2=\text{CF}_2$, CH_3CHF_2 , and CH_3CF_3 have been studied. As the sample size increased, the percentage hydrogenolysis decreased. More importantly, the C-F hydrogenolysis at temperatures ranging from 75° to 400°C was studied. The apparent activation energies and the A factors have been evaluated. They are summarized in Table 13 of this report. The E_a values range from 12 kcal mol^{-1} for $\text{CH}_3\text{CH}_2\text{F}$ to 26 kcal mol^{-1} for CH_3CHF_2 and CH_3CF_3 . Possible mechanisms for the C-F hydrogenolysis were also discussed.

Table 13
 Apparent E_a and A Factor Values
 for the Complete C-F Hydrogenolysis of Fluorocarbons

Compound	Slope	Apparent E_a (kcal mol ⁻¹) ^a	Intercept	A Factor (sec ⁻¹)
CH ₂ =CHF	-7685	15.3	15.825	3.73×10^7
CH ₃ CH ₂ F	-6154	12.2	11.670	5.85×10^5
CHF=CHF	-8774	17.4	16.503	7.34×10^7
CH ₂ =CF ₂	-10176	20.2	17.272	1.59×10^8
CH ₃ CHF ₂	-12964	25.8	22.309	2.44×10^{10}
CH ₃ CF ₃	-12854	25.5	19.073	9.60×10^8

C. List of Reprints Included with this Report

- DOE/ER/03898-47 "Formation of 1-Silacyclopenta-2,4-diene through Recoil Silicon Atom Reactions," E. E. Siefert, K.-L. Loh, R. A. Ferrieri, and Y.-N. Tang, J. Am. Chem. Soc., 102, 2285-2289 (1980).
- DOE/ER/03898-48 "Reactions of Silicon Atoms and Silylenes," a chapter in "Reaction Intermediates," vol. 2, (R. A. Abramovitch, ed.), Plenum Publishing Company Limited, Y.-N. Tang, (total 107 pages), already published in 1980. [Reprint is still not available. It will be sent in as soon as it arrives.]

D. List of Preprints Included with this Report

- DOE/ER/03898-49 "Unusual Compounds Synthesized via Nuclear Recoil Methods," Y.-N. Tang, a chapter in a volume of the ACS series, entitled, "Nuclear Applications in Biological, Environmental, and Pure Chemistry," (K. A. Krohn and J. W. Root, eds.), to be published in 1980. [This is a revised version of DOE/ER/03898-43]
- DOE/ER/03898-50 "Reactions of Monomeric Difluorosilylene with Ethylene," E. E. Siefert, S. D. Witt, and Y.-N. Tang, submitted to J. C. S., Chem. Comm., for publication.
- DOE/ER/03898-51 "Heterogeneous Hydrogenolysis of Some Fluorocarbons," S. D. Witt, E.-C. Wu, K.-L. Loh, and Y.-N. Tang, submitted to J. of Catalysis.

E. List of Presentations During this Period

- (1) "Heterogeneous Hydrogenation and Hydrogenolysis of Fluorocarbons,"
Y.-N. Tang, E.-C. Wu, and S. D. Witt, presented at the 179th
National ACS Meeting in Houston, Texas, March, 1980.
- (2) "Reactions of Monomeric Difluorosilylene with Ethylene,"
Y.-N. Tang and E. E. Siefert, presented at the ACS Combined
Regional Meeting, Southeast-Southwest, New Orleans, Louisiana,
December, 1980.