the limiting negative temperature dependence of $T^{-0.5}$ calculated from transition state theory for bimolecular reactions. By analogy with the olefin reactions, a reversible formation of an oxygen atom-sulfide complex could be postulated to account for the observed negative temperature dependence (eq 8 and 9). The

$$\mathrm{O} + \mathrm{RSR'} \underset{-a}{\overset{a}{\rightleftharpoons}} \text{complex} \tag{8}$$

$$\text{complex} \xrightarrow{b} \text{products} \tag{9}$$

products of the reactions $O + CH_3SCH_3$ and $O + CH_3SSCH_3$ are consistent with a mechanism involving addition of oxygen to sulfur, followed by fragmentation of the energy-rich adduct, which is discussed in detail in the accompanying paper.

The general nature of the complex could be similar to that suggested for the O + olefin reactions.[24] Transition-state theory can be used to adequately reproduce the observed Arrhenius behavior of plots of k_{298}/k_T if appropriate values are chosen for the two S–O bending frequencies, ω, in the transition state and for $E = E_a - E_{-a} + E_b$, as described previously.[24] Because a single pair of ω,E values does not provide a unique fit to the Arrhenius plots, reasonable values of ω are assumed, and the best value of E is then chosen to fit the experimental data. The bending frequencies[27] in gaseous $(CH_3)_2SO$ are 376 and about 333 cm^{-1}, which could be considered upper limits for the bending frequencies in the transition state. For the usual simplifying assumptions that both frequencies are identical and harmonic[24] for $O + CH_3SCH_3$, the pair of ω,E values, 200 cm^{-1} and −1300 cal mol^{-1}, leads to an adequate fit of the data, as does the pair 200 cm^{-1} and −1000 cal mol^{-1} for $O + CH_3SSCH_3$. If a higher value of ω were chosen, for example, 300 cm^{-1}, values of E would be −1100 and −800 cal mol^{-1} for CH_3SCH_3 and CH_3SSCH_3, respectively. The values of E required to fit the data are somewhat more negative than for the case of O + tetramethylethylene,[24] due in part to the restriction of lower S–O bending frequencies in the assumed sulfoxide structure of the transition state in comparison with the epoxide structure for the olefin reactions.

On the other hand, the curvature of the Arrhenius plots for the thiols ($T^{1.5}$ for CH_3SH and $T^{1.2}$ for C_2H_5SH) is about the maximum temperature dependence ($T^{1.5}$) of the preexponential factor allowed by transition-state theory.[24] Also, at least some of the curvature may be due to two concurrent mechanisms: addition to the sulfur atom and abstraction of hydrogen, which would be expected to have low and high activation energies, respectively. The hydrogen bound to sulfur is more weakly bound (92 kcal/mol;[28] on the basis of spectroscopic evidence, ≤87.4 kcal/mol[29]) and is expected to be more readily abstracted than the alkyl hydrogens (~94–98 kcal mol^{-1}). The product analysis experiments[20] indicate that abstraction may account for about 10% of the total reaction at 300 K, with addition of oxygen to sulfur followed by fragmentation of the adduct accounting for the remainder. If the temperature-dependent term, $A_2 \exp(-B/T)$, in the modified form of the Arrhenius expression for the thiols given in the Results [$k = A_1 + A_2 \exp(-B/T)$] is identified with the abstraction path, then at 300 K abstraction would make up 14% of the total calculated value of k, which is close to the value of 10% obtained from product analysis results. However, it should be emphasized that the particular functional form used was arbitrarily chosen in that it assumes a zero activation energy for one of the two routes.

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Gas-Phase Reactions of O(^{3}P) Atoms with Methanethiol, Ethanethiol, Methyl Sulfide, and Dimethyl Disulfide. 2. Reaction Products and Mechanisms[1]

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Abstract: In conjunction with the determinations of the rate constants of reactions of the ground-state oxygen atoms, O(^{3}P), with methanethiol, ethanethiol, methyl sulfide, and dimethyl disulfide described in the preceding paper,[3] a parallel study was carried out of the products and mechanisms of the same reactions at 300 K. Oxygen atoms were generated by the mercury-photosensitized decomposition of N_2O, used in large excess, and the recovered products were analyzed by gas chromatography. The total pressure was varied from 300 to 1200 torr. Nitrogen formed in the photosensitized decomposition of N_2O provided a direct measure of the number of O atoms generated and allowed determination of the yields of some of the products per oxygen atom reacting with the sulfur organic compounds. From a detailed analysis of the experimental results obtained with single sulfur organics and their mixtures, it is possible to derive substantial quantitative information on the reaction mechanisms. The postulated overall reaction mechanisms include some novel features common to the thiols, sulfide, and disulfide studied, which provide a simple explanation for some unexpected experimental trends observed.

Introduction

The present study of the products and mechanisms of the reactions of the ground-state oxygen atoms, O(^{3}P), with CH_3SH, C_2H_5SH, CH_3SCH_3, and CH_3SSCH_3 has been carried out in parallel with the determinations for the same reactions of the rate constants and Arrhenius parameters, described in the preceding paper.[3] There is no quantitative information in the literature on the mechanisms of these reactions, in spite of their relevance to some important industrial, environmental, and biochemical problems, although some useful qualitative information has been obtained.[4-6] Gutman and his co-workers have found an ap-

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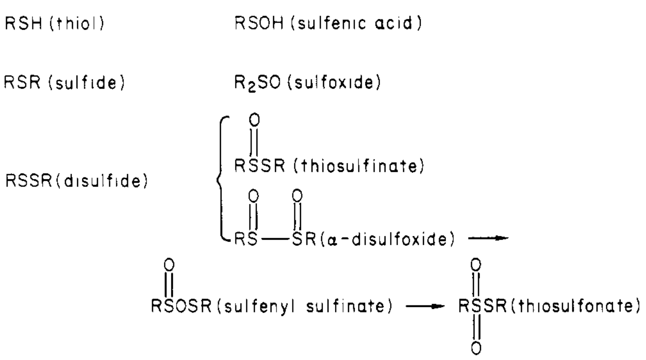
Chart I



proximate linear dependence of the activation energies of the O + RSH (where R represents CH_3 or C_2H_5) and O + CH_3SCH_3 reactions on the ionization potentials of the sulfur organics.[7] By analogy with the same relationship established earlier[8,9] for the O + alkene reactions, known[8] to proceed by O(^{3}P) *addition* to the alkenes, these authors have postulated essentially exclusive *addition* of O(^{3}P) to RSH and CH_3SCH_3 and consider, on the basis of "indirect evidence", that hydrogen *abstraction* reactions such as (in the case of RSH) eq 1 are only of minor importance

$$O + RSH \rightarrow OH + RS \qquad (1)$$

if they occur at all. In view of their qualitative observation in crossed molecular jet experiments at very low pressures (10^{-2}–10^{-3} torr) of mass numbers corresponding to R, RSO, and RSOH in the O + RSH reaction and to CH_3, CH_3O, and CH_3S in the O + CH_3SCH_3 reaction, they have postulated the primary reactive routes[5] shown in eq 2 and 3. Formation of RSOH in eq 2 and

$$\begin{aligned} O + RSH \rightarrow [RS(O)H]^* &\xrightarrow{(M)} RSOH \\ &\rightarrow R + HSO \\ &\rightarrow H + RSO \qquad (2) \end{aligned}$$

$$\begin{aligned} O + CH_3SCH_3 \rightarrow [CH_3S(O)CH_3]^* &\xrightarrow{(M)} (CH_3)_2SO \\ &\rightarrow CH_3 + CH_3SO \\ &\rightarrow CH_3O + CH_3S \qquad (3) \end{aligned}$$

of $(CH_3)_2SO$ in eq 3 is assumed to occur by collisional stabilization of some of the initial energy-rich adducts at the low pressures of 10^{-2}–10^{-3} torr used in the crossed-jet experiments. These postulates will be discussed in the light of the experimental results obtained in the present study, together with some aspects of the very recent paper by Kirchner, Vettermann, and Indruch,[6] who identified by high-resolution mass detection and related techniques a number of products formed in the reactions of O(^{3}P) with several alkane thiols.

The types of organic sulfur compounds used in the present study and some of their oxygenated derivatives of interest are shown in Chart I.

Experimental Section

Atomic oxygen, O(^{3}P), was produced by mercury-photosensitized decomposition of N_2O at 253.7 nm with a low-pressure mercury lamp and a Corning 9-54 filter to remove the 184.9-nm line. The reactions involved are as follows:

$$Hg6(^1S_0) + h\nu\ (253.7\ \text{nm}) \rightarrow Hg6(^3P_1)$$

$$Hg6(^3P_1) + N_2O \rightarrow Hg6(^1S_0) + N_2 + O(^3P) \qquad (4)$$

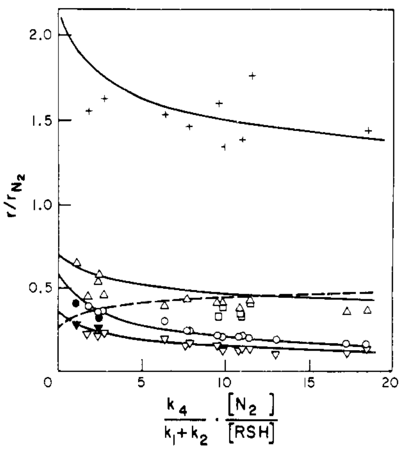


Figure 1. Rates of product formation and reactant consumption relative to N_2, r/r_{N_2}, as a function of the yield of N_2 (or reaction time) for the reactions of O(^{3}P) atoms with thiols. For O(^{3}P) + CH_3SH: ▽, H_2; ○, CH_4; □, H_2O; △, CH_3SSCH_3; +, CH_3SH. For O(^{3}P) + C_2H_5SH: ▼, H_2; ●, C_2H_6. The lines are the results of computer simulation of the mechanism in Table VI, with the dashed line representing H_2O.

The reaction mixture (Hg, N_2O, sulfur organic) had to be circulated continuously through the quartz reaction cell (diameter 50 mm, length 100 mm) and a small connecting U-tube containing a drop of mercury in order to replenish the mercury vapor removed in the cell by reaction with the products. Direct photolysis of the sulfur compounds was believed not to be significant under these conditions. The intensity of the transmitted 253.7-nm light was measured with a monochrometer, photomultiplier, and recorder in order to determine the relative concentration of Hg during an experiment. In preliminary static experiments in which the reactants were not circulated, a severe decrease of the mercury concentration was indicated by an increased transmission of the 253.7-nm light, and the results were not reproducible.

The products not condensable at 77 K were collected by a Toepler pump and measured manometrically. Ethane was separated from the condensible products at 96 K, added to the noncondensible fraction, and determined by difference. Hydrogen also was determined by difference after removal of ethane at 77 K and combustion of the noncondensable fraction on CuO. The remaining gases, N_2 and CH_4, were analyzed by gas chromatography using a column of 2% squalane on alumina. In some experiments, ethane was determined also by gas chromatography along with N_2 and CH_4. This procedure gave values for ethane in good agreement with the manometric method. Aliquots of the condensable fraction were analyzed by gas chromatography using a stainless-steel column packed with Porapak QS, a thermal conductivity detector, and propane as an internal standard. The results of at least three aliquots were averaged for each run.

The reactants were thoroughly degassed prior to their use. Their source and purity levels are given in the accompanying paper.[3]

Results

Methanethiol. The time dependence of the yield of the major products observed in the O + CH_3SH reaction at 25 °C (H_2, CH_4, CH_3SSCH_3) is shown in Table I. Static experiments (Table IA) show that as the reaction proceeds, there is a pronounced decrease in the rate of N_2 formation (r_{N_2}) and a simultaneous increase in the H_2/CH_4 ratio. The decrease in r_{N_2} signifies a decrease in the rate of photodecomposition of N_2O; it is found to be accompanied by an increase in the transmission of the 253.7-nm Hg resonance line and is explained by partial removal of Hg vapor by its reaction with the products. Even a very minor occurrence of this last reaction may cause efficient Hg depletion since [Hg] is very small (2×10^{-3} torr at 25 °C). In circulating experiments (Table IB,C), on the other hand, both r_{N_2} and the H_2/CH_4 ratio remain approximately independent of irradiation time, and no increase in the transmission of the 253.7-nm line is observed. The gradual decrease in the yields of H_2 and CH_4 in the course of the reaction (Table IB) is explainable by progressive accumulation in the reaction products of the much faster reacting CH_3SSCH_3 and its effective competition with CH_3SH for O atoms. Support for this view is provided by the experiments with initially added CH_3SSCH_3 (Table IC) in which H_2 and CH_4 yields are further suppressed while their ratio is essentially unaltered. The trends

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Table I. Time Dependence of the Yields of Some of the Products Observed in the Reaction of O(^{3}P) Atoms with Thiols (RSH) at 25 °C

	amt of reactants,[a] torr		irradn time,	r_{N_2},[b]	r/r_{N_2}[b,c]					H_2/ CH_4	
run	N_2O	RSH	min	μmol/min	H_2	CH_4	C_2H_6	RSSR	−ΔRSH	ratio	$(r_{RH}/r_{N_2})_0$[d]
				(A) RSH = CH_3SH. Static Experiments							
31	659.7	15.7	5	0.68	0.36	0.39		nd	nd	0.94	
32	657.7	12.1	10	0.61	0.40	0.32		0.7	3.0	1.20	
30	658.2	13.0	90	0.19	0.81	0.32		nd	nd	2.54	
				(B) RSH = CH_3SH. Circulating Experiments							
40	585.2	12.0	5	1.11	0.22	0.39		0.45	1.6	0.57	0.53
46	561.6	12.7	7.5	1.03	0.21	0.35		0.54	nd	0.60	0.55
36	586.8	12.1	7.5	1.11	0.23	0.36		0.46	1.6	0.62	0.55
33	590.5	11.6	15	1.20	0.19	0.30		0.39	1.5	0.61	0.59
44	590.5	12.9	22.5	1.08	0.17	0.24		nd	nd	0.68	nd[c]
38	588.2	13.3	22.5	1.11	0.17	0.24		0.43	1.5	0.69	0.54
45	586.8	12.6	45	1.06	0.11	0.17		0.36	nd	0.68	0.57
35	588.4	12.5	45	1.11	0.14	0.16		0.36	1.4	0.87	0.50
				(C) RSH = CH_3SH. Circulating Experiments with Additives							
53[e]	587.8	11.8	12	0.95	0.08	0.11		0.41	0.6	0.71	
41[f]	585.9	12.1	15	1.00	0.11	0.02		0.7	2.6	6	
				(D) RSH = C_2H_5SH. Circulating Experiments							
118	594.3	18.9	10	0.74	0.28	0.005	0.41	~0.65[g]	~2.6[g]		0.55
116	571.7	17.4	20	0.74	0.25	0.004	0.33	~0.58	nd		0.53

[a] Reactant pressures are in torr at 25 °C. The corresponding total amounts in the reaction cell in micromoles are obtained by multiplying by 15.15. [b] r_{N_2} = rate of N_2 formed in micromoles per minute = rate of production of O atoms; r/r_{N_2} = yield of the product per one O atom produced. [c] nd = not determined. A blank entry indicates absence (0.00 value) of the product. [d] Approximate initial values of r_{RH}/r_{N_2} (derived as outlined in the Discussion). RH is CH_4 in part B (for O + CH_3SH) and C_2H_6 in part D (for O + C_2H_5SH). [e] CH_3SSCH_3 1.46 torr (22.1 μmol) added initially. [f] About 3 torr (~46 μmol) of O_2 added initially. [g] Some $CH_3SSC_2H_5$ was formed by thermal disproportionation with $C_2H_5SSC_2H_5$ of CH_3SH impurity (about 1%) in the C_2H_5SH used. After approximate allowance for this, the value for $C_2H_5SSC_2H_5$ becomes ~0.7, and that for $-\Delta C_2H_5SH \approx 2.0$.

Table II. Effect of Pressure on the Yields of the Products Observed in the Reaction at 25 °C of O Atoms with CH_3SH[a]

	amt of reactants,[b] torr		r_{N_2},[b] μmol/	r/r_{N_2}[b]					H_2/ CH_4	
run	N_2O	CH_3SH	min	H_2	CH_4	$(CH_3S)_2$	H_2O	$-\Delta CH_3SH$	ratio	$(r_{CH_4}/r_{N_2})_0$[c]
91	281.9	11.00	0.823	0.15	0.21	0.41	0.33	1.6	0.72	0.53
85	310.9	10.02	0.865	0.13	0.20	0.42	0.41	1.8	0.68	0.55
90	587.5	10.20	0.873	0.13	0.22	0.35	0.33	1.4	0.61	0.54
84	589.6	9.28	0.928	0.11	0.19	nd	nd	nd	0.55	nd
87	935.0	11.17	0.874	0.13	0.21	0.41	0.39	1.3	0.62	0.52
86	1185.9	10.62	0.875	0.12	0.21	0.37	0.35	1.7	0.58	0.54

[a] Irradiation time 30 min. [b] The symbols and the units used are explained in the footnotes *a–c* in Table I. [c] See footnote *d* in Table I.

in the results in Table IB,C are presented graphically in Figure 1 and will be discussed in a later section.

At a constant irradiation time of 30 min but at a varying pressure of N_2O (from about 280 to 1180 torr) no significant variation in r_{N_2} or the yields of the products is observed at 25 °C, as shown in Table II. There appears to be a slight decrease in the H_2/CH_4 ratio with increasing partial pressure of N_2O, which can be explained in a simple manner, as will be discussed later. Table II also gives the results of the gas chromatographic determinations of the H_2O yields, expressed as r_{H_2O}/r_{N_2}. Correction for the "background" water, based on two dark runs, amounted to close to 20% of the total observed. In view of this and the difficulties inherent in the recovery and quantitative determination of small amounts of water, it is possible that the yields of water may be subject to an appreciable systematic error.

Ethanethiol. Only a few experiments were carried out to determine whether the mechanism of the O + C_2H_5SH reaction is similar to that of O + CH_3SH. The major products are H_2 and $C_2H_5SSC_2H_5$, along with a trace of CH_4, as shown in Table ID. The average ratio of H_2 to C_2H_6 is 0.72, similar to that for H_2 and CH_4 in the O + CH_3SH reaction. The trace of CH_4 is probably a product of the reaction of O atoms with the CH_3SH impurity in the C_2H_5SH.

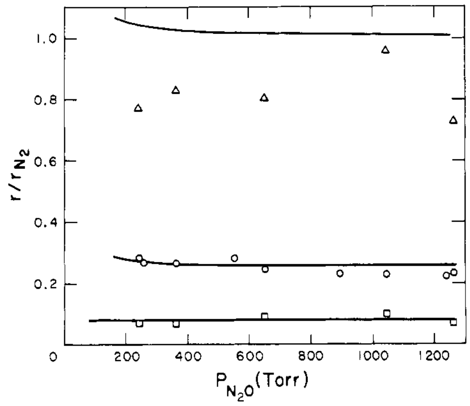


Figure 2. Rates of product formation and reactant consumption relative to N_2, r/r_{N_2}, as a function of the pressure of N_2O in the O(^{3}P) + CH_3SCH_3 reaction: □, $(CH_3)_2SO$; ○, C_2H_6; △, CH_3SCH_3. The lines are the results of computer simulation of the mechanism in Table VIIA,B.

Methyl Sulfide. The yields of the main products, C_2H_6 and $(CH_3)_2SO$, observed in the reaction of O atoms with CH_3SCH_3 alone are given in Table IIIA. There appears to be a slight pressure dependence of the rate of formation of C_2H_6 and $(CH_3)_2SO$, as shown in Figure 2, for pressures between 255 and 1273 torr, but the variation is very small and close to the potential experimental uncertainty. In the presence of C_2H_5SH (Table IIIB), i.e., when about an equal amount of C_2H_5SH is added to CH_3SCH_3 (such that on the average about 5% of the O atoms react with C_2H_5SH), the major observed products are CH_4, $CH_3SSC_2H_5$, and $C_2H_5SSC_2H_5$, with smaller amounts of H_2 and C_2H_6, while $(CH_3)_2SO$ is apparently absent. (In these experi-

Table III. Yields of Some of the Products Observed in the Reaction at 25 °C of O Atoms with CH_3SCH_3 Alone and with C_2H_5SH Added to CH_3SCH_3[a]

run	amt of reactants,[a] torr: N_2O	CH_3SCH_3	C_2H_5SH	r_{N_2},[a] μmol/min	r/r_{N_2}[a-c]: H_2	CH_4	C_2H_6	$(CH_3)_2SO$	MSSM	MSSE	ESSE	−MSM	$r^*_{C_2H_6}/r_{N_2}$[d]	$r^*_{CH_4}/r_{N_2}$[e]
					(A) Experiments without Additives									
80	243.2	11.5		0.98			0.282	0.07	0.038			0.77	0.25	
72	256.0	9.43		0.98			0.271	nd	0.033			nd	0.25	
76	362.1	10.7		1.00			0.267	0.07	0.019			0.83	0.25	
74	553.0	9.04		1.03			0.283	nd	0.013			nd	0.27	
78	650.0	8.08		1.01			0.245	0.09	0.009			0.80	0.24	
75	893.8	9.14		1.01			0.232	nd	0.014			nd	0.23	
77	1046.2	8.07		1.03			0.228	0.10	0.007			0.96	0.22	
73	1239.3	9.58		1.01			0.222	nd	0.008			nd	0.22	
79	1261.6	11.4		0.99			0.231	0.07	0.008			0.73	0.23	
					(B) Experiments with C_2H_5SH Initially Added									
122	591.0	15.6	21.4	0.69	0.17	0.83	0.056			0.30	0.79	nd		0.87
123	588.9	17.4	13.1	0.75	0.09	0.87	0.032			0.31	0.76	nd		0.88
124	587.6	14.4	14.7	0.76	0.10	0.84	0.038			0.32	0.71	nd		0.89
125	567.5	14.0	14.6	0.73	0.11	0.84	0.038			0.29	0.72	nd		0.88
116	571.7		17.4	0.74	0.25	0.004	0.328			0.01	0.58	nd		

[a] The symbols and the units used are explained in the footnotes a–c in Table I. The irradiation time is 30 min in part A and 20 min in part B. [b] MSSM = CH_3SSCH_3; MSSE = $CH_3SSC_2H_5$; ESSE = $C_2H_5SSC_2H_5$; −MSM = $-\Delta CH_3SCH_3$. [c] r_{CH_3SH}/r_{N_2} is negligible in A; it is approximately 0.13 ± 0.07 in B, where the large uncertainty range is due to the CH_3SH impurity of about 1% in the C_2H_5SH used. [d] $r_{C_2H_6}/r_{N_2}$ values after correction (as outlined in the Discussion) for the minor additional formation of CH_3 in the quenching reaction $Hg6(^3P_1) + CH_3SCH_3 \rightarrow Hg6(^1S_0) + CH_3 + CH_3S$. [e] r_{CH_4}/r_{N_2} values after correction (as outlined in the Discussion) for the minor side reactions affecting this ratio: the quenching of $Hg6(^3P_1)$ by CH_3SCH_3 and the small consumption of O atoms in reaction with the C_2H_5SH added and the $C_2H_5SSC_2H_5$ and $CH_3SSC_2H_5$ formed.

Table IV. Some Products Observed in the Reactions of Oxygen Atoms with (A) CH_3SSCH_3, (B) Mixtures of CH_3SSCH_3 with CH_3SH, and (C) Mixtures of CH_3SSCH_3 with C_2H_5SH[a]

run	amt of reactants,[b] torr: $(CH_3S)_2$	thiol	thiol/$(CH_3S)_2$, %	irradiatn time, min	r_{N_2},[c] μmol/min	r/r_{N_2}[c,d]: H_2	CH_4	C_2H_6	MSH	ESH	MSSM	MSSE	ESSE	% O atom reaction with thiol
						(A) CH_3SSCH_3								
92	1.96	0	0	15	0.94						−0.8			0
112	7.73	0	0	20	0.71						−0.4			0
						(B) Mixtures of CH_3SSCH_3 with Methanethiol								
111	9.30	6.8	42.3	20	0.64	0.02	0.05		−0.8		−1.0			1.3
109	9.54	16.9	63.9	5	0.60	0.08	0.12		−1.0		−2.1			3.0
110	7.56	15.0	66.5	20	0.63	0.05	0.08		−0.7		−0.1			3.4
93	1.96	8.7	81.6	15	0.85	0.05	0.08		−1.0		−0.2			7.2
94	1.23	9.6	88.7	30	0.85	0.06	0.09		−1.2		0.2			12.0
40	0	12.0	100	5	1.11	0.22	0.39		−1.2		0.45			100
						(C) Mixtures of CH_3SSCH_3 with Ethanethiol								
121	7.36	14.6	66.5	30	0.62	0.04	0.05	0.03	2.9	−3.4	−2.6	2.7	0.4	4.6
119	7.63	16.8	68.8	10	0.62	0.06	0.06	0.04	6.7	−8.0	−6.4	6.4	0.8	5.0
117	6.48	19.2	74.8	20	0.61	0.07	0.06	0.05	4.2	−5.2	−3.8	3.6	0.8	6.7
118	0	18.9	100	10	0.74	0.28	0.005	0.41		−2.6		0.05	0.8	100

[a] Temperature 25 °C. Oxygen atoms are produced by mercury-photosensitized reaction of 590 ± 4 torr N_2O (551 torr N_2O in run no. 109). [b] Reactant pressures are in torr at 25 °C and can be converted into micromoles by multiplying by 15.15. The thiol is CH_3SH in B and C_2H_5SH in C. [c] See footnotes *b* and *c* in Table I. [d] MSH = CH_3SH; ESH = C_2H_5SH; MSSM = CH_3SSCH_3; MSSE = $CH_3SSC_2H_5$; ESSE = $C_2H_5SSC_2H_5$.

ments, $\Delta(CH_3)_2S$ and ΔC_2H_5SH could not be determined because of their similar GC retention times.) The yield of C_2H_6, which is much smaller than that obtained either with CH_3SCH_3 or C_2H_5SH alone, together with the large yields of CH_4, $C_2H_5SSC_2H_5$, and the a priori unexpected $CH_3SSC_2H_5$ as well as the absence of $(CH_3)_2SO$, provides useful mechanistic information, as will be discussed.

Dimethyl Disulfide. The reaction of O atoms with CH_3SSCH_3 gives no gaseous products, as shown in Table IVA. If CH_3SH is added (so that 1–12% of the O atoms react with the thiol, Table IVB), H_2 and CH_4 are produced to a greater extent than expected from the percentage reaction of O atoms with CH_3SH. With the addition of C_2H_5SH (so that about 5% of O atoms react with C_2H_5SH, Table IVC), the usual products of the O + C_2H_5SH reaction are observed, although in greater yields than expected for the amount of reaction of O atoms with C_2H_5SH. Also, CH_3SH and $CH_3SSC_2H_5$ are formed in large yields (but are at best formed only in trace amounts with either CH_3SSCH_3 or C_2H_5SH alone). Furthermore, the rates of consumption of CH_3SSCH_3 and C_2H_5SH are greatly accelerated relative to those in the separate reactions. These large effects are primarily due to an extensive thermal "disproportionation" reaction between CH_3SSCH_3 and C_2H_5SH. When these two reactants are mixed, significant quantities of CH_3SH, $CH_3SSC_2H_5$, and $C_2H_5SSC_2H_5$ are formed even without irradiation, as shown in Table V.

Discussion

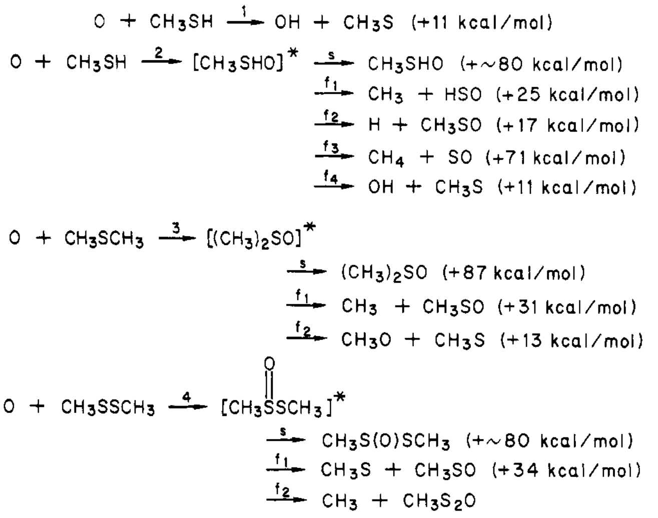
As in the earlier studies of the reactions of oxygen atoms with simple sulfur organics, in the present work also it was not possible to recover, identify, and quantitatively measure, with the techniques employed, all products in order to obtain a satisfactory material balance. This is at least in part due to the well-known

Table V. Thermal "Disproportionation" Reactions between CH_3SSCH_3 and C_2H_5SH (Dark Runs)

run	amt of reactants,[a] torr (μmol)			amt of products,[b] μmol					matl balance,[c] %	
	$(CH_3S)_2$	C_2H_5SH	N_2O	MSH	ESH	MSSM	MSSE	ESSE	ΔCH_3S	ΔC_2H_5S
145	7.45 (112.9)	12.8 (193.9)	426.2	18.4	175.5	99.4	14.6	1.2	+1.9	+0.2
147	8.70 (131.9)	20.1 (304.0)	592.1	17.2	282.2	119.3	14.0	0.8	+1.2	−1.1
149	6.80 (103.1)	19.7 (297.8)	591.4	20.8	275.0	88.0	16.7	1.5	+2.3	−0.2

[a] See footnote a in Table I. [b] MSH = CH_3SH; ESH = C_2H_5SH; MSSM = CH_3SSCH_3; MSSE = $CH_3SSC_2H_5$; ESSE = $C_2H_5SSC_2H_5$. [c] Material balance of the CH_3S and C_2H_5S groups recovered in the products, i.e., the difference between their final and initial amounts expressed as percentages of the initial amounts.

Scheme I



low stability and elusive character frequently associated with simple oxygenated sulfur organics. Also, the difficulty inherent in quantitative recovery from vacuum systems and measurement of relatively small amounts of water, an obvious potential product of oxidation reactions of this kind, has already been mentioned. However, in spite of these limitations, it appears possible to draw far-reaching mechanistic conclusions from a detailed analysis of the results of the present work.

The set of elementary reactions shown in Scheme I, with the approximate estimates[10,11] of their exothermicities (i.e., of the $-\Delta H^\circ_{298}$ values), provides a suitable framework for a quantitative discussion of the primary steps in the reactions studied. Reactions s (2s, 3s, and 4s) are collisional stabilizations of the energy-rich initial adducts, while reactions f are the potential channels for their fragmentation (or "displacement") reactions.

The above set of primary reactions includes the reactive routes proposed qualitatively by Lee et al.[4] and by Slagle et al.[5] and a number of other reactions which are estimated to be thermodynamically feasible and should be considered. Examples of the latter are, in particular, the hydrogen abstraction reaction (eq 1), proposed here (at room temperature) only for the thiols, and the addition–stabilization and two addition–fragmentation channels for the O + CH_3SSCH_3 reaction.

Adequate understanding of the reaction mechanisms also requires, besides the quantitative information on the primary reactive routes, a knowledge of the secondary reactions of the free radicals formed in the primary steps. It is evident that the free radicals expected to be formed in these systems are to a large extent the same in all the O + sulfur organic reactions studied, so that some of the major secondary reactions should be qualitatively similar. It is convenient to go into the details of the secondary free-radical processes while discussing individual O + sulfur organic reactions.

O + CH_3SH Reaction. A basic question in this case and in other O + thiol reactions is whether hydrogen abstraction (eq 1) occurs and, if it does, whether it is the exclusive primary step. If abstraction occurs exclusively and if, as is likely, OH radicals react with simple thiols only by the very fast abstraction reaction shown in eq 5, all oxygen atoms would be converted into H_2O. Water

$$OH + RSH \rightarrow H_2O + RS \qquad (5)$$

is formed in the O + CH_3SH reaction, but its observed yield per oxygen atom (r_{H_2O}/r_{N_2}) is well below unity (Table II). It appears, therefore, that although abstraction is not the exclusive primary process, it may occur at least to some extent.[12] However, a quantitative estimate of the importance of abstraction cannot be based on the measured yields of H_2O alone (Table II) because of the analytical difficulties in its quantitative determination, mentioned earlier, and the consequent need to use relatively large conversions, at which secondary reaction of O atoms with the very reactive disulfide formed by combination of CH_3S radicals (eq 6) becomes very important. Furthermore, water may be also formed in reactions other than reaction 1, as will be discussed.

$$CH_3S + CH_3S \rightarrow CH_3SSCH_3 \qquad (6)$$

An estimate of the relative importance of the primary reaction channels in the O + CH_3SH reaction can be obtained from the rates of formation of CH_4 and H_2. Addition of small amounts of O_2 (run 41, Table IC) suppresses almost completely CH_4 production and decreases strongly the yield of H_2, indicating that these compounds are formed in reactions 7 and 8. Less efficient

$$CH_3 + CH_3SH \rightarrow CH_4 + CH_3S \qquad (7)$$

$$H + CH_3SH \rightarrow H_2 + CH_3S \qquad (8)$$

scavenging of H may be ascribed to the smaller rate of the H + O_2 + M reaction ($k = 5.5 \times 10^{-32}$ cm^6 molec^{-2} s^{-1}; M = N_2)[13] relative to $CH_3 + O_2 + M$ ($k = 2 \times 10^{-31}$ cm^6 molec^{-2} s^{-1}; M = N_2).[13]

The observed relatively large yields of CH_4 and H_2 and their suppression by small amounts of O_2 show qualitatively that the addition–fragmentation reaction channels $2f_1$ and $2f_2$ constitute a substantial part of the primary reaction process and that molecular formation of CH_4 (eq $2f_3$) is unimportant. It is also postulated, as will be discussed later, that the adduct stabilization channel (eq 2s) is unimportant under the present experimental conditions. As already mentioned, addition–fragmentation channel $2f_4$ is, in the present work, indistinguishable from the hydrogen abstraction reaction 1 and will be treated as abstraction and not considered separately. Thus, the only primary reaction channels postulated are hydrogen abstraction (eq 1) and the two addition–fragmentation channels (eq $2f_1$ and $2f_2$).

In the reaction system used in the present study, N_2 and $O(^3P)$ atoms are formed in equal amounts in the mercury-photosensitized decomposition of N_2O, i.e.

$$Hg6(^3P_1) + N_2O \rightarrow Hg6(^1S_0) + N_2 + O(^3P) \qquad (q_{N_2O})$$

in competition with

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(10) Benson, S. W. *Chem. Rev.* **1978**, *78*, 23–35.

(11) Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley: New York, 1976.

(12) The OH radicals (and therefore H_2O) can result from reaction 1 or via the addition–fragmentation reaction channel $2f_4$. The two alternatives are indistinguishable in the present work although, in principle, reaction $2f_4$ should be suppressed at sufficiently high pressures (probably higher than those in the experiments in Table II and Figure 2) while reaction 1 should not. In the present discussion, "abstraction" signifies the sum of reactions 1 and $2f_4$.

(13) Hampson, R. F., Jr.; Garvin, D. *NBS Spec. Publ.* (*U.S.*) **1977**, *No. 513*.

$$\mathrm{Hg6(^3P_1) + RSR' \rightarrow Hg6(^1S_0) + products} \qquad (q_{RSR'})$$

where RSR′ stands for the sulfur organic compounds studied and their reaction products. N_2O is always present in huge excess, and the extent of the last reaction (eq $q_{RSR'}$) amounts typically only to about 4–5%, for which correction is readily made when necessary. Since N_2O does not react in any other way under the experimental conditions used, the ratios r/r_{N_2} of the rates of product formation represent normalized rates per atom produced. With minor corrections for any interfering secondary or side reactions, these ratios then provide direct information on the extents of the different primary reaction channels.

For the O + CH_3SH reaction studied, it is necessary to determine what corrections to r_{CH_4}/r_{N_2} and r_{H_2}/r_{N_2} are required to allow for the following three interfering secondary and side reactions: (1) quenching of $Hg6(^3P_1)$ atoms by CH_3SH (eq $q_{RSR'}$, with RSR′ = CH_3SH); (2) direct photolysis of CH_3SH; (3) secondary reaction of O atoms with the very reactive CH_3SSCH_3 product (formed in eq 6). These three processes will be briefly discussed.

(1) At the very large N_2O/CH_3SH ratios used, we estimate that, in the experiments in Table I, only 4–5% of the $Hg6(^3P_1)$ atoms are quenched by CH_3SH. This leads to a slight additional formation of H but not of CH_3. In agreement with this estimate, a more than fourfold variation in N_2O/CH_3SH in Table II increases only slightly H_2 at larger CH_3SH/N_2O ratios, where the quenching by CH_3SH is expected to be somewhat increased. It is important to note that in these experiments, only the yields of H_2 are affected and not, within the experimental error, those of CH_4. No correction for the quenching by CH_3SH is therefore required for r_{CH_4}/r_{N_2} while r_{H_2}/r_{N_2} should be decreased by a small amount which can be calculated.

(2) As already mentioned, partial removal of mercury vapor by reaction with products at longer reaction times in static experiments, measured by increased transmission of the 253.7-nm mercury resonance line, caused appreciable direct photolysis of CH_3SH, accompanied by increased H_2/CH_4 ratios (Table IA). The increase in the H_2/CH_4 ratio is explained by the much larger quantum yield of H (0.93) than of CH_3 (0.07) in the direct photolysis of CH_3SH.[14] In the circulating experiments in Tables I and II, on the other hand, in which Hg vapor is continuously replenished, no increase in the transmission of the 253.7-nm light is observed and the H_2/CH_4 ratio is only about 0.6. Although it is believed that, under these conditions, direct photolysis of CH_3SH is relatively unimportant, it may nevertheless occur to a small extent. However, the effect of allowing for photolysis would be mainly to reduce somewhat the observed yield of H_2 while, in view of the large H_2/CH_4 ratio in direct photolysis, it would leave the yields of CH_4 essentially unaltered.

(3) Secondary consumption of O atoms in the rapid reaction with the CH_3SSCH_3 product leads to a pronounced decrease in r_{CH_4}/r_{N_2} and r_{H_2}/r_{N_2} with increasing conversion, as shown in Table IB and Figure 1. It is therefore necessary to obtain the values of these two quantities in the limit of zero conversion, $(r_{CH_4}/r_{N_2})_0$ and $(r_{H_2}/r_{N_2})_0$. Approximate values $(r_{CH_4}/r_{N_2})_0 \approx 0.5$ and $(r_{H_2}/r_{N_2})_0 \approx 0.25$ are indicated by visual extrapolation to N_2 = 0 of the experimental data in Figure 1.

Considerably better values of $(r_{CH_4}/r_{N_2})_0$ can be obtained by applying the steady-state treatment to oxygen atoms (which are consumed in reactions 1, 2, and 4 only). As a first approximation, it can be assumed that the relative yield of CH_3SSCH_3 is constant, i.e., that $[CH_3SSCH_3]/[N_2] \approx \alpha$, where α is assumed to be a constant independent of time (or N_2) as is shown in Table I and Figure 1 to be roughly the case. With this approximation, eq I

$$\frac{[\mathrm{CH_4}]}{[\mathrm{N_2}]} = \frac{k_{2f_1}}{k_1 + k_2}\,\frac{\ln\,(1 + b\alpha[\mathrm{N_2}])}{b\alpha[\mathrm{N_2}]} \qquad \text{(I)}$$

can be written, where $b = k_4/((k_1 + k_2)[CH_3SH])$. The value of $k_4/(k_1 + k_2) = 57$ at room temperature, obtained in the preceding paper,[3] has been used in the calculation from eq I of $k_{2f_1}/(k_1 + k_2)$ (i.e., of $(r_{CH_4}/r_{N_2})_0$). The values obtained, given in Tables I and II, are only approximate because the assumption that $[CH_3SSCH_3]/[N_2]$ is independent of N_2 is only approximately true. Nevertheless, reasonably consistent values of $(r_{CH_4}/r_{N_2})_0$ are obtained for all experimental points, independent of reaction time. This shows that the decline in CH_4/N_2 with reaction time can be adequately accounted for by the secondary consumption of O atoms in reaction with the CH_3SSCH_3 product. It also provides additional support for the value of the $k_4/(k_1 + k_2)$ ratio based on the values of the rate constants in the preceding paper. A more precise verification of this was obtained by detailed analysis of the overall reaction mechanism using the steady-state treatment and also by computer simulation[15] without imposing the steady-state restriction, as outlined in the following.

Table VI. Elementary Reactions Involved in the Reaction of $O(^3P)$ Atoms with CH_3SH and Used in the Steady-State Treatment and Computer Simulation

reaction no.	reaction
	(A) $O(^3P)$ Atom Production
	$Hg6(^1S_0) + h\nu(253.7\ nm) \rightarrow Hg6(^3P_1)$
	$N_2O + Hg6(^3P_1) \rightarrow Hg6(^1S_0) + N_2 + O(^3P)$
	(B) Mechanism of the $O(^3P) + CH_3SH$ Reaction
1	$O(^3P) + CH_3SH \rightarrow OH + CH_3S$
$2f_1$	$O(^3P) + CH_3SH \rightarrow CH_3 + HSO$
$2f_2$	$O(^3P) + CH_3SH \rightarrow H + CH_3SO$
4	$O(^3P) + CH_3SSCH_3 \rightarrow CH_3S + CH_3SO$
5	$OH + CH_3SH \rightarrow H_2O + CH_3S$
6	$CH_3S + CH_3S \rightarrow CH_3SSCH_3$
7	$CH_3 + CH_3SH \rightarrow CH_4 + CH_3S$
8	$H + CH_3SH \rightarrow H_2 + CH_3S$
9	$CH_3S + CH_3SO \rightarrow CH_3S(O)SCH_3$
10	$CH_3SO + CH_3SO \rightarrow CH_3S(O)OSCH_3 \rightarrow CH_3S(O)_2SCH_3$
11	$CH_3SO + HSO \rightarrow$ products
12	$HSO + HSO \rightarrow$ products
13	$CH_3S + HSO \rightarrow CH_3SH + SO$
14	$CH_3S(O)SCH_3 + CH_3SH \rightarrow CH_3SSCH_3 + CH_3SOH$
15	$CH_3SOH + CH_3SH \rightarrow CH_3SSCH_3 + H_2O$
	(C) Minor Thiol Decomposing Reactions
q_{CH_3SH}	$CH_3SH + Hg6(^3P_1) \rightarrow Hg6(^1S_0) + H + CH_3S$
ϕ_{CH_3SH}	$CH_3SH + h\nu(253.7\ nm) \rightarrow H + CH_3S$

The overall reaction mechanism which had to be postulated for the O + CH_3SH reaction in order to explain the trends in the products observed is summarized in Table VI. The set of the corresponding differential rate equations can be solved by applying the steady-state treatment to the atoms and free radicals involved and assuming that $CH_3S(O)SCH_3$ and CH_3SOH are consumed in reactions 14 and 15. The solutions giving concentrations of products as a function of time are complicated and will not be given here since they were found to give the same results as the numerical integrations on a computer. The lines in Figure 1 represent the optimized results of the computer simulations for the set of reactions in Table VI. One of the main objects of the simulation has been to determine the relative rate constants of the primary rate channels for the O + CH_3SH reaction by matching the observed and the calculated trends in product yields as a function of time. The best agreement was obtained with a $k_1{:}k_{2f_1}{:}k_{2f_2}$ ratio of 0.1:0.6:0.3.

For the two minor thiol decomposition reactions (Table VIC), it was assumed that $r_{q,CH_3SH}/r_{q,N_2O} \approx 0.03$ and $I_{a,CH_3SH}/I_{a,Hg} \approx 0.03$. The first ratio assumes that $k_{q,CH_3SH}/k_{q,N_2O} = 2$, which is a reasonable value by analogy with the known[16] ratio of $k_{q,C_2H_5SH}/k_{q,N_2O}$. The second ratio is based on the known[14] value $\epsilon(CH_3SH) = 44.6$ L mol^{-1} cm^{-1} and an assumed value of ϵ(Hg) = 9×10^6 in the same units, which was found to be suitable for the computer simulations, although the results were not particularly sensitive to the choice of the value. The value of ϵ(Hg)

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is uncertain because of varying degrees of self-reversal of the resonance line among low-pressure mercury lamps.[17,18] The value adopted is within a factor of about 2 of that reported for somewhat similar low-pressure mercury lamps. Reactions 5, 7, and 8 are assumed to occur very fast so that $r_5 = r_1$, $r_7 = r_{2f_1}$, and $r_8 = r_{2f_2}$.

For the radical–radical reactions 6 and 9–13, only ratios of rate constants are important. Statistical ratios $k_7 = k_9 = k_{11} = k_{13} = 2k_6 = 2k_{10} = 2k_{12}$ are assumed. Only one final product is indicated in these reactions, the one which is believed to be the most likely final product of the reaction. In reaction 6, disproportionation of CH_3S radicals is omitted since it appears to be of little importance.[14,19,20] In reaction 9, the most probable product is[21] the thiosulfinate shown in Table VI. Similarily in reaction 10, the most stable product appears to be[22] the thiosulfonate. The products of reactions 11 and 12 are not known; we make the reasonable assumption that they do not affect significantly the products observed. Reaction 13 is a plausible reaction responsible for some regeneration of CH_3SH. Although CH_3S and HSO could perhaps react also to some extent in a manner analogous to reaction 9, such a refinement of the reaction mechanism would not be warranted at this time, and reaction 13 alone is retained. SO formed in reaction 13 would probably tend to polymerize or react with mercury and would therefore be difficult to observe in the present reaction system.

Postulation of an important role for reactions 14 and 15 in the mechanism of the O + CH_3SH reaction is dictated by the observation that the yield of CH_3SSCH_3 remains quite large even at long reaction times although $O(^3P)$ atoms react with CH_3SSCH_3 at room temperature about 60 times faster than with CH_3SH. If there is not a regeneration path for the CH_3SSCH_3 attacked by O atoms, the relative rate of CH_3SSCH_3 formation, $r_{CH_3SSCH_3}/r_{N_2}$, in the O + CH_3SH reaction would have to decline very rapidly at longer reaction times, in the same manner as r_{CH_4}/r_{N_2} declines. The regeneration path involves the reaction of CH_3SO radicals (formed in reactions $2f_2$ and $4f_1$) with CH_3S radicals to produce $CH_3S(O)SCH_3$, which then interacts via reactions 14 and 15 with two molecules of CH_3SH to form two molecules of CH_3SSCH_3 and one molecule of H_2O. If reactions 14 and 15 are excluded from the reaction mechanism in Table VI, computer simulation shows that the relative yield $r_{CH_3SSCH_3}/r_{N_2}$ would have to decline rapidly and be as low as 0.1 at $b[N_2] = 4$ and 0.03 at $b[N_2] = 15$ in Figure 1, in contrast to the observed values of about 0.5 and 0.4, respectively. Reactions analogous to reactions 14 and 15 are known to occur,[23] and their involvement in the mechanism of the O + CH_3SH reaction is quite plausible. Furthermore, they are required in a similar way for the understanding of some aspects of the O + CH_3SCH_3 and O + CH_3SSCH_3 reaction systems studied, as will be shown below.

It is evident from Figure 1 that product yields predicted by computer simulation are in reasonable agreement with the observed yields. This computer simulation leads to the ratio of rate constants $k_1:k_{2f_1}:k_{2f_2}$ of 0.1:0.6:0.3, mentioned above. The relative value of 0.6 for $k_{2f_1}/(k_1 + k_2)$ has the lowest uncertainty (probably less than 0.05) since the CH_4 yield is not affected significantly by any side reactions (other than reaction 4). The sum of the rate constant ratios $k_1/(k_1 + k_2)$ and $k_{2f_2}/(k_1 + k_2)$ therefore has to be close to 0.4. The value of $k_{2f_2}/(k_1 + k_2)$ is largely determined by the observed yield of hydrogen (r_{H_2}/r_{N_2}), and $k_1/(k_1 + k_2)$ is then essentially established by difference ($k_1/(k_1 + k_2) = 0.4 - k_{2f_2}/(k_1 + k_2)$). As discussed above, there is some uncertainty regarding the amount of the additional H atoms produced by direct photolysis of CH_3SH, and this introduces a corresponding uncertainty in $k_{2f_2}/(k_1 + k_2)$ and therefore also in $k_1/(k_1 + k_2)$. The extreme possible values of $k_{2f_2}/(k_1 + k_2)$ seem to be close to 0.3 and 0.4. In view of this, the ratios of the three rate constant fractions could vary between 0.1:0.6:0.3 and 0:0.6:0.4. The former (0.1:0.6:0.3) appear to be in best agreement with the experimental trends, and we believe that they are the more probable ratios. They are also in agreement with the value $k_1/(k_1 + k_2) = 0.14$ at 300 K, which can be calculated from the modified Arrhenius expression for the rate constant of the O + CH_3SH reaction obtained in the preceding paper.[3]

The general conclusion of Slagle et al.[5] that addition of $O(^3P)$ to CH_3SH is the major primary step in the O + CH_3SH reaction at room temperature is corroborated in the present work. The present results provide as well a quantitative assessment of the relative importance of the competing reaction channels and indicate that abstraction, although minor, may contribute as much as about 10% to the total rate. However, the CH_3SOH adduct detected by Slagle et al. at the extremely low pressure of 10^{-2}–10^{-3} torr is difficult to rationalize as a primary product of the reaction. The present results indicate that the stabilization reaction (eq 2s), if it occurs at all, is very minor. This is understandable since the reaction is ~80 kcal/mol exothermic, and the S–C bond dissociation energy, D(S–C), in the adduct is expected to be greatly weakened, perhaps down to 53 kcal/mol, by analogy with the decline in D(S–C) from 77 to 55 kcal/mol[10] on addition of O to CH_3SCH_3 to form $(CH_3)_2SO$. Stabilization of the adduct in the O + CH_3SH reaction is therefore expected to be very inefficient even at 600 torr in the present work, and a substantial stabilization at a pressure as low as 10^{-2}–10^{-3} torr would be difficult to understand.

Kirchner et al.[6] studied the O + CH_3SH reaction, but because of the possible secondary O atom free radical reactions such as, for example, $CH_3S + O \rightarrow CH_3 + SO$, they could not draw firm conclusions regarding the mechanism of the reaction. Secondary O atom free radical reactions of this type are not important in the present work because of the very small concentrations of oxygen atoms ($<10^9$ atoms/cm^3) in the presence of more than an 8 orders of magnitude greater concentration of CH_3SH and the large value of $k_1 + k_2$.

O + C_2H_5SH Reaction. To compare the ethanethiol and the methanethiol reactions with $O(^3P)$ atoms, two experiments were carried out with C_2H_5SH alone (Table ID) and several with its mixtures with CH_3SCH_3 (Table IIIB) and with CH_3SSCH_3 (Table IVC). Apart from H_2O, the yield of which was not determined, the main products observed in the O + C_2H_5SH reaction are H_2, C_2H_6, and $C_2H_5SSC_2H_5$. These products are analogous to those in the O + CH_3SH reaction but with C_2H_6 and $C_2H_5SSC_2H_5$ replacing CH_4 and CH_3SSCH_3, as expected, and, moreover, the yields of the corresponding products in the two reactions are similar (Table I and Figure 1). The reaction mechanism appears therefore to be very similar for the two thiols.

O + CH_3SCH_3 Reaction. The products of the $O(^3P)$ + CH_3SCH_3 reaction (Table IIIA) show the absence of H_2 and CH_4 and appreciable yields of ethane ($r_{C_2H_6}/r_{N_2} \approx 0.25$) and of dimethyl sulfoxide ($r_{(CH_3)_2SO}/r_{N_2} \approx 0.1$), as well as small amounts of CH_3SSCH_3. The consumption of CH_3SCH_3 per O atom is slightly below unity, although the mean (0.82) of the values in Table IIIA is subject to an appreciable analytical error. In the experiments in Table IIIB, with C_2H_5SH added to provide readily abstractable hydrogen, the character of the reaction drastically changed, although only a few percent of the O atoms reacted with C_2H_5SH. Appreciable amounts of H_2 and large amounts of CH_4 are formed while the yield of C_2H_6 is nearly completely suppressed and $(CH_3)_2SO$ and CH_3SSCH_3 are eliminated. In addition, besides the expected large yield of $C_2H_5SSC_2H_5$, considerable amounts of the a priori unexpected $CH_3SSC_2H_5$ are also formed. Although determination of water proved to be difficult because of its large background, the measurements indicated at best only a small yield.

The mechanism required to explain these results is summarized in Table VII. The primary reaction step is addition of O atoms to CH_3SCH_3, but of the three possible reaction channels indicated earlier (eq 3s, $3f_1$, and $3f_2$) only the addition–fragmentation channel $3f_1$ appears to be important and is included in Table VII.

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Table VII. Elementary Reactions Involved in the Reaction of O(^{3}P) Atoms with CH_3SCH_3 and with Mixtures of CH_3SCH_3 and C_2H_5SH

reaction no.	reaction
(A) Mechanism of the O(^{3}P) + CH_3SCH_3 Reaction	
3f$_1$	$O(^3P) + CH_3SCH_3 \rightarrow CH_3 + CH_3SO$
10	$CH_3SO + CH_3SO \rightarrow CH_3S(O)OSCH_3 \rightarrow CH_3S(O)_2SCH_3$
16	$CH_3 + CH_3 \rightarrow C_2H_6$
17a	$CH_3 + CH_3SO \rightarrow (CH_3)_2SO$
17b	$CH_3 + CH_3SO \rightarrow CH_3SOCH_3$
(B) Minor Side Reactions in A	
$q_{CH_3SCH_3}$	$CH_3SCH_3 + Hg6(^3P_1) \rightarrow Hg6(^1S_0) + CH_3 + CH_3S$
9	$CH_3S + CH_3SO \rightarrow CH_3S(O)SCH_3$
18	$CH_3S + CH_3 \rightarrow CH_3SCH_3$
19[a]	$2CH_3S(O)SCH_3 \rightarrow CH_3SSCH_3 + CH_3S(O)_2SCH_3$
(C) Mechanism of the O(^{3}P) + CH_3SCH_3 Reaction with C_2H_5SH Added	
3f$_1$	$O(^3P) + CH_3SCH_3 \rightarrow CH_3 + CH_3SO$
10	$CH_3SO + CH_3SO \rightarrow CH_3S(O)OSCH_3 \rightarrow CH_3S(O)_2SCH_3$
20	$CH_3 + C_2H_5SH \rightarrow CH_4 + C_2H_5S$
21	$C_2H_5S + C_2H_5S \rightarrow C_2H_5SSC_2H_5$
22	$C_2H_5S + CH_3SO \rightarrow CH_3S(O)SC_2H_5$
23	$CH_3S(O)SC_2H_5 + C_2H_5SH \rightarrow C_2H_5SSC_2H_5 + CH_3SOH$
24	$CH_3SOH + C_2H_5SH \rightarrow CH_3SSC_2H_5 + H_2O$
(D) Minor Side Reactions in C[b]	
$q_{C_2H_5SH}$	$C_2H_5SH + Hg6(^3P_1) \rightarrow Hg6(^1S_0) + H + C_2H_5S$
$\phi_{C_2H_5SH}$	$C_2H_5SH + h\nu(253.7\ nm) \rightarrow H + C_2H_5S$

[a] This reaction may be very slow under the present experimental conditions.[21] [b] In addition to $q_{CH_3SCH_3}$ (given in B) and reaction of about 5% of the O atoms with C_2H_5SH, as discussed in the text.

For the reaction of O(^{3}P) with CH_3SCH_3 alone, the mechanism given in Table VIIA is very simple and involves initial formation of only two free radicals, CH_3 and CH_3SO. Ethane is formed by combination of CH_3 radicals. For comparison of its expected yield, based on the mechanism in Table VIIA, with the experimental values in Table III, the latter have to be corrected for the additional minor formation of CH_3 in the quenching of Hg6($^3P_1$) by CH_3SCH_3. The corrected $r^*_{C_2H_6}/r_{N_2}$ values are given by eq II, with the ratio of the quenching rate constants of CH_3SCH_3

$$\frac{r^*_{C_2H_6}}{r_{N_2}} = \frac{r_{C_2H_6}}{r_{N_2}} - \frac{1}{4}\frac{k_{q,CH_3SCH_3}}{k_{q,N_2O}}\frac{[CH_3SCH_3]}{[N_2O]} \qquad (II)$$

and N_2O taken[16] as $k_{q,CH_3SCH_3}/k_{q,N_2O} = 2.4$. As a result of the very small $[CH_3SCH_3]/[N_2O]$ ratios used, the corrections have varied from only 0.005 to less than 0.03. The corrected values, $r^*_{C_2H_6}/r_{N_2}$, are given in Table IIIA. Their mean value is 0.24, which, when compared with the statistically expected value of 0.25, suggests that reaction 3f$_1$ may account for as much as 95–100% of the primary step in the O + CH_3SCH_3 reaction.

Besides CH_3, equal amounts of CH_3S are also formed in the quenching of Hg6($^3P_1$) by CH_3SCH_3 and appear to be entirely responsible for the small amounts of CH_3SSCH_3 observed (Table IIIA). In the presence of much larger and mutually very similar concentrations of CH_3 and CH_3SO, formation of CH_3SSCH_3 by direct dimerization of CH_3S must be ruled out. The plausible path involves the known[21] reactions 9 and 19. From approximate steady-state considerations, it would be expected that $r_{CH_3SSCH_3}/r_{N_2} = 0.25 r_{q,CH_3SCH_3}/r_{q,N_2O}$ (which is given by the positive value of the last term in eq II), in agreement with the data in Table IIIA and displaying the expected trend of larger values at smaller $[CH_3SCH_3]/[N_2O]$ ratios, at which Hg6($^3P_1$) quenching by CH_3SCH_3 is greater. The results of some computer simulations based on the mechanism of CH_3SSCH_3 formation given in Table VIIB were consistent with experimentally observed yields.

Formation of CH_3S with equal amounts of CH_3O has been postulated[5] in the second fragmentation channel (reaction 3f$_2$) of the initial adduct. However, the dimer of CH_3S (i.e., CH_3SSCH_3) is formed only in trace amounts and, as mentioned, can be explained by the CH_3S formed in the quenching of Hg6($^3P_1$) by CH_3SCH_3. Also, GC analysis of the products formed when C_2H_5SH is added to CH_3SCH_3 showed only an extremely small peak with retention time close to that of methanol, the compound expected to be produced if CH_3O is present. It appears, therefore, that fragmentation channel 3f$_2$ can be at best only of a relatively minor importance under the present experimental conditions.

Formation of dimethyl sulfoxide in the reaction of O(^{3}P) with CH_3SCH_3 alone seems to result from combination of CH_3 with CH_3SO (reaction 17a) and not from collisional stabilization of the initial adduct (reaction 3s). This conclusion is based on the observation that $(CH_3)_2SO$ is not formed when CH_3 radicals are efficiently scavenged by adding C_2H_5SH (Table IIIB). In the absence of C_2H_5SH, the statistically expected sum of the yields of $(CH_3)_2SO$ and CH_3SOCH_3 is 0.50. The observed value of $(CH_3)_2SO/N_2$ is only about 0.1 which would seem to indicate, barring some unknown analytical difficulties, that reaction 17b is more efficient than reaction 17a. Unfortunately, it is not possible to draw firm conclusions in this respect since no information seems to be available on these two reactions and on the stability and chemical behavior of CH_3SOCH_3. Disproportionation of CH_3 and CH_3SO appears to be unimportant since no CH_4 was formed in the experiments in Table IIIA.

The mechanism of the O + CH_3SCH_3 reaction in the presence of added C_2H_5SH is summarized in Table VIIC, with some minor reactions in sections B and D (which include the quenching of Hg6($^3P_1$) by CH_3SCH_3 and by C_2H_5SH and direct photolysis of the latter). All CH_3 radicals may be expected in this case to react with C_2H_5SH to form CH_4, but the observed values of CH_4 have to be corrected for the CH_3 formed in the quenching of Hg6($^3P_1$) by CH_3SCH_3 and those of N_2 for the small (about 5%) reaction of O(^{3}P) with C_2H_5SH and with the $C_2H_5SSC_2H_5$ and $CH_3SSC_2H_5$ products formed. The two corrections partially cancel, and the net effect is to increase slightly the observed r_{CH_4}/r_{N_2} to the corrected r_{CH_4}/r_{N_2} values in the last column of Table IIIB. In as much as all CH_3 radicals are scavenged in these experiments by C_2H_5SH and converted into CH_4, the mean of the four r_{CH_4}/r_{N_2} values indicates that the CH_3-generating addition–fragmentation channel 3f$_1$ accounts for close to 90% of the primary step in the O + CH_3SCH_3 reaction. Within the experimental uncertainty, this is in agreement with the estimate of 95–100% based on the $r_{C_2H_6}/r_{N_2}$ values in Table IIIA. Reaction 3f$_1$ is therefore by far the most important and may perhaps be the exclusive primary reaction channel.

In the O + CH_3SCH_3 reaction in the presence of C_2H_5SH (Table IIIB), the small yield of C_2H_6 ($r_{C_2H_6}/r_{N_2} \approx 0.04$) is explained by the ~5% O atom reaction with C_2H_5SH and abstraction of H from C_2H_5SH by the C_2H_5 radicals thus formed. The yield of H_2 ($r_{H_2}/r_{N_2} \approx 0.1$) is largely and perhaps entirely explainable by the minor quenching reaction of Hg6($^3P_1$) by C_2H_5SH and perhaps also by a small amount of direct light absorption by C_2H_5SH, as discussed earlier for the analogous case of CH_3SH. The following additional primary fragmentation of the adduct

$$O + CH_3SCH_3 \rightarrow [(CH_3)_2SO]^* \rightarrow CH_3S(O)CH_2\cdot + H\cdot$$

can be ruled out because $CH_3S(O)CH_2\cdot$ radicals would abstract H from the C_2H_5SH added to form $(CH_3)_2SO$, but the sulfoxide is not observed in this case (Table IIIB). Furthermore, the fragmentation reaction would probably be endothermic and unlikely to occur. Minor formation of CH_3S by the quenching of Hg6($^3P_1$) by CH_3SCH_3 has already been discussed. In the presence of the C_2H_5SH added, CH_3S radicals are scavenged to form CH_3SH. As pointed out in footnote *c* of Table III, formation of CH_3SH is observed, but the analytical uncertainty is large

Table VIII. Elementary Reactions Involved in the Reaction of $O(^3P)$ Atoms with CH_3SSCH_3 and with Mixtures of CH_3SSCH_3 and CH_3SH

reaction no.	reaction
	(A) Mechanism of the O + CH_3SSCH_3 Reaction
$4f_1$	$O(^3P) + CH_3SSCH_3 \rightarrow CH_3S + CH_3SO$
4s	$O(^3P) + CH_3SSCH_3 + M \rightarrow CH_3S(O)SCH_3 + M$
6	$CH_3S + CH_3S \rightarrow CH_3SSCH_3$
9	$CH_3S + CH_3SO \rightarrow CH_3S(O)SCH_3$
10	$CH_3SO + CH_3SO \rightarrow CH_3S(O)OSCH_3 \rightarrow CH_3S(O)_2SCH_3$
19	$2CH_3S(O)SCH_3 \rightarrow CH_3SSCH_3 + CH_3S(O)_2SCH_3$
	(B) Major Additional Reactions with CH_3SH Present in A
14	$CH_3S(O)SCH_3 + CH_3SH \rightarrow CH_3SSCH_3 + CH_3SOH$
15	$CH_3SOH + CH_3SH \rightarrow CH_3SSCH_3 + H_2O$

because of a CH_3SH impurity of about 1% in the C_2H_5SH used.

Formation of large amounts of $CH_3SSC_2H_5$ ($r_{CH_3SSC_2H_5}/r_{N_2} \approx 0.30$) in the O + CH_3SCH_3 reaction in the presence of added C_2H_5SH (Table IIIB) is a priori unexpected, but it provides important information about the overall reaction mechanism. Its presence as a reaction product requires the postulate of special reaction paths. Reactions 22–24 postulated in Table VIIC are entirely analogous to reactions 10, 14, and 15 which had to be postulated earlier (Table VIB) to explain the trends in the products of the O + CH_3SH reaction. In fact, occurrence of reactions 22–24 is demanded, by analogy, if reactions 10, 14, and 15 are incorporated into the mechanism of the O + CH_3SH reaction. Formation of $CH_3SSC_2H_5$ is then readily explained (reaction 24). If all O atoms react with CH_3SCH_3 in reaction $3f_1$ and all CH_3 radicals react then with the C_2H_5SH added (reaction 20), CH_3SO and C_2H_5S would be formed in equal amounts and would be removed from the system by mutual interactions (reactions 10, 21, and 22). Neglecting minor reactions, one would expect then on statistical grounds that $r_{C_2H_5SSC_2H_5}/r_{N_2} \approx 0.75$ and $r_{CH_3SSC_2H_5}/r_{N_2} \approx 0.50$. The values actually observed are approximately 0.75 and 0.30. On comparison of the expected and the observed yields, it should be born in mind that the yields of these two compounds may be affected to some extent by thermal "disproportionation" reactions of the type shown in Table V, which would tend in this case to decrease the amount of $CH_3SSC_2H_5$ and increase that of $C_2H_5SSC_2H_5$.

O + CH_3SSCH_3 Reaction. The reaction of O atoms with CH_3SSCH_3 is characterized by a remarkable absence of any products which could be observed by the analytical techniques used in the present study (Table IVA). In particular, such products as H_2, CH_4, C_2H_6, and CH_3SH (as well as C_2H_5SH) are not formed. The consumption of CH_3SSCH_3 per O atom, $r_{CH_3SSCH_3}/r_{N_2}$, appears to be appreciably smaller than unity: the mean of two determinations is 0.6 ± 0.2, but, as a consequence of the low volatility of CH_3SSCH_3, the precision of the combined manometric/GC technique used has been poor, and the mean value is subject to a large uncertainty.

Although the experimental information obtained on the reaction of O atoms with CH_3SSCH_3 alone and its mixtures with CH_3SH and C_2H_5SH (Table IV) is limited, it is possible to postulate for it a plausible reaction mechanism, summarized in Table VIII, by extrapolating the mechanisms proposed above for the O + CH_3SH and O + CH_3SCH_3 reactions. The postulated relatively simple mechanism, given by the primary reaction 4 followed by the secondary reactions 6, 9, 10, and 19, appears to be consistent with the experimental information available at present. In the case of the reaction of O with CH_3SSCH_3 alone (Table IVA), it can explain lack of products observable by the analytical techniques used and the small degree of consumption of CH_3SSCH_3. It receives support from the experiments with CH_3SSCH_3 mixtures with thiols, as will be discussed. Nevertheless, the mechanism is not necessarily unique and is clearly only tentative.

In view of the large exothermicity of addition of O atoms to CH_3SSCH_3 and the low strength of the critical SS and probably also SC bonds, it is likely that fragmentation reactions (reactions 4f) of the energy-rich primary adduct are much faster than its collisional stabilization (reaction 4s) under the conditions employed. The predominant and perhaps the exclusive fragmentation channel probably involves fission of the SS bond only (reaction $4f_1$). However, absence of CH_4 and C_2H_6 in the reaction of O atoms with CH_3SSCH_3 alone (Table IVA) does not necessarily rule out formation of CH_3 radicals since they may conceivably add to CH_3SSCH_3 under the experimental conditions used rather than combine to form C_2H_6 or abstract from CH_3SSCH_3 to form CH_4. At the same time, the small yields of CH_4 obtained in the presence of either added CH_3SH or C_2H_5SH (Tables IVB,C, respectively) suggest that CS fission (reaction $4f_2$) is of relatively minor importance, if it occurs at all. Nevertheless, both in the presence of CH_3SH (Table IVB) and of C_2H_5SH (Table IVC) the yields of CH_4, although small, are somewhat larger than expected for the small reaction of O atoms with the thiol added. In the case of CH_3SH addition to CH_3SSCH_3, the observed yields of CH_4 are decreased appreciably but are not reduced to zero after correction for the CH_4 contribution from the 1–12% O + CH_3SH reaction which takes place. In the case of C_2H_5SH, the corresponding correction would be relatively small. It appears, therefore, that small amounts of CH_3 are probably formed, corresponding roughly to about 5% of the O atoms generated. This would set an upper limit on reaction $4f_2$ at about 5% but would not prove its occurrence since CH_3 could perhaps result from some secondary processes such as $Hg6(^3P_1)$ quenching by CH_3SSCH_3.

In the O + CH_3SSCH_3 experiments with CH_3SH added as a free-radical scavenger (Table IVB), the most conspicuous result is the relatively large consumption of CH_3SH ($r_{CH_3SH}/r_{N_2} \approx -1$), although only 1–12% of the O atoms reacted with CH_3SH. This unexpected result can be readily explained by invoking once again reactions 14 and 15 (Tables VIB and VIIIB), since the statistical probability of $CH_3S + CH_3SO$ combination (reaction 9) is 0.5, and two CH_3SH molecules are consumed for each $CH_3S(O)SCH_3$ formed in reaction 9. Thus in all the three types of reactions studied, O + CH_3SH, O + CH_3SCH_3, and O + CH_3SSCH_3, there has always been a need to postulate the occurrence of reactions 14 and 15, or their equivalents, to explain a very unusual or unexpected experimental observation. These reactions (or possibly some related sulfur organic reactions with a similar final outcome) have provided in each case a simple explanation of seemingly paradoxical results. This does not, of course, diminish the need for further efforts to observe directly, when feasible, the products of these reactions which could not be observed by the techniques used in the present study.

The large changes in the concentrations of CH_3SSCH_3, CH_3SH, and C_2H_5SH and the large formation of $CH_3SSC_2H_5$ in Table IVC are due to the rapid thermal "disproportionation" between CH_3SSCH_3 and C_2H_5SH, as demonstrated by the data in Table V, obtained without irradiation by the 253.7-nm mercury resonance light. Unfortunately, the disproportionation reaction obscures some of the trends which might have been useful as further indicators of the course of the O + CH_3SSCH_3 reaction. Disproportionation between CH_3SSCH_3 and CH_3SH, on the other hand, simply regenerates the same two compounds in the same amounts and therefore does not interfere with the data in Table IVB.

Thermal "Disproportionation" between CH_3SSCH_3 and C_2H_5SH. This reaction has been only of incidental interest in the present work and has not been investigated in any detail. However, a very brief discussion of the data in Table V has a bearing on the study of the O + CH_3SSCH_3 reaction in the presence of C_2H_5SH (Table IVC). Regardless of the finer details of the mechanism of disproportionation, the process observed can be represented by the following two equilibrating reactions:

$$C_2H_5SH + CH_3SSCH_3 \rightleftarrows CH_3SH + C_2H_5SSCH_3$$

$$C_2H_5SH + C_2H_5SSCH_3 \rightleftarrows C_2H_5SSC_2H_5 + CH_3SH$$

The CH_3S and C_2H_5S groups are transferred intact. It was therefore possible to count them in the initial reactants and in

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the products and obtain their material balances which are listed in the last two columns of Table V, where they are expressed as percentages of the initial amounts. The very small differences indicate reasonable analytical precision and no loss of material in the course of the thermal disproportionation. The differences are nevertheless sufficiently large to preclude quantitative analysis for the much less extensive concentration changes specifically due to the O atom reactions in the experiments listed in Table IVC.

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^{13}C–^{1}H Coupling Constants in Carbocations. 3.[1] Variation of ΔJ with Electron Demand in Aryldialkyl Carbocations

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Abstract: One-bond ^{13}C–H coupling constants for groups adjacent to the cationic center have been measured for 3-arylnortricyclyl (**1**), 1-aryl-1-cyclopropylethyl (**2**), 2-arylnorbornyl (**3**), 1-aryl-1-methylethyl (**4**), and 1-arylcyclopentyl (**5**) carbocations. The differences ΔJ between $^{1}J_{CH}$ in the cations and those in neutral, model ketones are linearly dependent upon electron demand at the cationic carbon as measured by σ^+ constants. Combination of this relationship and the original ΔJ equation gives a new equation for aryldialkyl carbocations which relates ΔJ to both the dihedral angle between the C–H orbital and the vacant p orbital and the electron demand at the cationic carbon, $\Delta J = (1 + 0.6\sigma^+)(10.9 - 14.3\cos^2\theta)$.

We have previously examined the applicability of one-bond ^{13}C–^{1}H coupling constants ($^{1}J_{CH}$) as a criterion for structure determination in a range of alkyl carbocations.[1] In static, classical, tertiary, alkyl cations we have shown that J_{CH} of groups adjacent to the cationic carbons differ from those in appropriate, neutral model compounds (ketones) by an amount depending upon the dihedral angle θ between the C–H bond and the unoccupied p orbital.[1] This dependency is given by

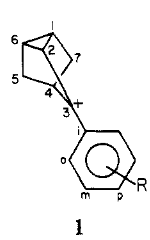
$$\Delta J = A - B\cos^2\theta \qquad (1)$$

where ΔJ is the J_{CH} value in the cation less that in a model ketone, A is the maximum inductive enhancement of J_{CH} (22.5 Hz), and B is the maximum hyperconjugative diminution of J_{CH} (33.1 Hz). Thus a maximum enhancement of J_{CH} occurs for ions where $\theta = 90°$ (+22.5 Hz) and an actual diminution of J_{CH} where $\theta = 0°$ (≤ -10Hz). For ions where $\theta = 30°$, for example, C_2–H of 1-methylcyclopentyl and C_3–H of 2-methylnorbornyl cations, no difference is observed from the values of cyclopentanone and 2-norbornanone, respectively.[1] Recent INDO-FPT calculations of Pachler and Pachter confirm the validity of the general form of our equation, although the calculated values of the constants are somewhat less than our experimental ones.[2]

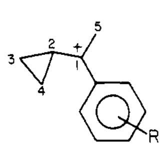
Equation 1 was derived from data for static, tertiary methyl carbocations in which a "full" positive charge was considered to reside on the cationic carbon and the A term was therefore considered to be a measure of the inductive effect of a "full" charge. The obvious extension of our systematic investigation was thus to measure J_{CH} as a function of charge density at the adjacent cationic carbon. We now report the results of this investigation for cations **1**–**5** where the aryl group provides a controlled variation in the electron demand at the cationic center which can be quantified by the appropriate Hammett substituent constant.

Results and Discussion

The use of aryl substituents to vary the charge density at an attached cationic carbon in a controlled fashion is well documented both for solvolytic studies[3] and for NMR studies in superacids.[4-6]



1



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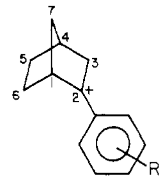

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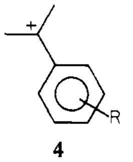

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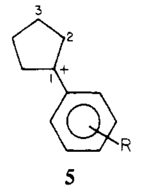

5

The choice of substituent constant to quantify this variation in charge density is critical, as has recently been demonstrated for ^{13}C shift correlations of cations in superacids.[7] For the groups adjacent to the cationic center in ions **1**–**5**, we have used both Brown's σ^{+}[8] and a substituent constant $\sigma^{\alpha C^+}$, derived from the methyl carbon shifts of a range of meta- and para-substituted 1-methyl-1-phenylethyl cations (**4**) generated in $HSO_3F/SbF_5/SO_2ClF$.[9]

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(9) The values of $\sigma_p^{\alpha C^+}$ are MeO −1.29, Me −0.49, F −0.24, Cl −0.07, Br −0.1, and CF_3 0.70; $\sigma_m^{\alpha C^+}$ CF_3 0.51, derived from the least-squares analysis of meta and para cations **4** ($\Delta\delta(CH_3) = 4.12\sigma^{\alpha C^+}$ r 0.990, SD 0.22). Brown, H. C.; Kelly, D. P.; Periasamy, M. *J. Org. Chem.*, in press.

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