kept in a constant-temperature water bath at 30 °C. After temperature equilibration, 50 μL of the stock solution of the imidate ester (0.01 M) in acetonitrile was added to the buffer solution by means of a Gilson Pipetman adjustable pipet (delivery range 0-200 μL). The reaction mixture was thoroughly stirred and kept at 30 °C for at least 10 half-lives of reaction before assay.

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C–C Bond Homolysis in $(CF_3S)_3C–C(SCF_3)_3$ at Room Temperature. Thermodynamic, Kinetic, and Electron Spin Resonance Results[1]

A. Haas,[2] K. Schlosser,*[2] and S. Steenken*[3]

Contribution from the Lehrstuhl für Anorganische Chemie II, Ruhr-Universität Bochum, D-4630 Bochum, West Germany, and Institut für Strahlenchemie im Max-Planck-Institut für Kohlenforschung, D-4330 Mülheim, West Germany.

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Abstract: In benzene solution at 10–60 °C $(CF_3S)_3C–C(SCF_3)_3$ undergoes a reversible homolytic C–C cleavage reaction to yield $(CF_3S)_3\dot{C}$ radicals which were identified by ESR. From the dependence of the stationary concentration of $(CF_3S)_3C$ on temperature the C–C bond dissociation energy is determined to be 13.7 kcal/mol. At 30 °C the equilibrium constant for C–C homolysis is 7.5×10^{-10} M. The change in free entropy occurring on C–C homolysis corresponds to 3.6 eu. The activation energy and entropy for C–C bond cleavage are 21.0 kcal/mol and 7.5 eu, respectively. The experimental results concerning the facile C-C homolysis are interpreted essentially in terms of sterically induced destabilization of the C–C bond in $(CF_3S)_3C$-$C(SCF_3)_3$.

Since the discovery by Lankamp, Nauta, and MacLean in 1968 that the triphenylmethyl radical on dimerization does not yield hexaphenylethane but a cyclohexadiene-type compound,[4] attempts have been made[5-9] to produce true ethanes that—by virtue of their voluminous or radical-stabilizing substituents—tend to undergo facile C–C homolysis at relatively low temperatures. As shown by Seebach et al.[6,7] with hexakis(aryl- or alkylthio)ethanes, homolytic dissociation of the C- C bond is detectable in the temperature range 55–110 °C.[10]

During systematic investigations of the photochemistry of perfluorothioketones, $(CF_3S)_2CS$ was also irradiated. During this photolysis, besides 1,1,3,3-tetrakis(trifluoromethylmercapto)thiirane and $CF_3S_nCF_3$, $(CF_3S)_3CC(SCF_3)_3$[11] was also formed. The present paper describes thermodynamic and kinetic results concerning the homolysis of hexakis(trifluoromethylmercapto)ethane in solutions near room temperature.

Experimental Section

A. Materials. Hexakis(trifluoromethylmercapto)ethane. In a quartz vessel equipped with stirrer and condenser, a solution of 9.8 g (0.04 mol) of $(CF_3S)_2CS$[12] in 400 mL of hexane was irradiated for 10 h at reflux temperature in a Rayonet photoreactor with UV light of 300 nm. The photolysis reaction was controlled by analyzing samples for the amount of unreacted starting material using the 500-nm band of $(CF_3S)_2CS$ for detection. The reaction was stopped at 90% conversion of $(CF_3S)_2CS$. On cooling to −70 to −80 °C white crystals of $(CF_3S)_2CC(SCF_3)_3$ deposited. After filtration the crystals were washed with hexane and recrystallized from ether: yield 1.6 g (18%); mp 129–130 °C (sealed tube); sublimation at 90 °C; IR (RbBr pellet) 1210 (s), 1170 (vs), 1085 (vs), 761 (s), 747 (m), 620 (w), 560 (w), 556 (m), 546 (m), 468 (m), 445 (w), 425 (m), 355 (m), 335 cm^{-1} (vw); ^{19}F NMR (in 90% CCl_3F) (CF_3) 36.9 ppm. Anal. Calcd for $C_8F_{18}S_6$: C, 15.13; S, 30.34. Found: C, 15.24; S, 30.51.

Benzene (Uvasol, Merck) was dried with sodium and used without further purification. Nitrogen and argon (99.997%) were purified with Oxisorb filters (Messer-Griesheim) (after purification O_2 content <0.1 vpm; H_2O content 0.5 vpm). Galvinoxyl (Aldrich) was recrystallized from carbon tetrachloride and stored at −30 °C under nitrogen. 2-Phenylbis(biphenylene)allyl[13] was recrystallized from benzene and isolated as a 1:1 adduct with benzene. For galvinoxyl and 2-phenylbis(biphenylene)allyl the free-radical content was determined spectrophotometrically using previously reported extinction coefficients.[13,14]

B. ESR Measurements. The ESR measurements were performed using a Varian E-9 ESR spectrometer with a variable-temperature unit. For double integration of the spectra the ESR spectrometer was connected to a DEC PDP 10 computer. The doubly integrated spectra of $\dot{C}(SCF_3)_3$ in benzene[15] were compared with corresponding data

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from 10^{-5}-10^{-4} *m* solutions of diphenylpicrylhydrazyl (DPPH) in benzene using the method described by Zimmermann et al.[16] The optical density of the DPPH solutions was determined using a Zeiss PMQ 2 spectrometer. The extinction coefficient at 519 nm of DPPH in benzene was taken to be 1.415×10^4 M^{-1} cm^{-1}.[16] The coupling constants and *g* factors were determined from simultaneous measurements of field and microwave frequency taking account of the difference in field between the ESR cell and NMR probe positions. The coupling constants and *g* factor are accurate to 30 mG and 5×10^{-5}, respectively.

C. Kinetic Measurements. Reaction rates of tris(trifluoromethylmercapto)methyl radicals in benzene with the scavenger radicals galvinoxyl and 2-phenylbis(biphenylene)allyl were determined by monitoring the decrease in the optical absorptions of the scavengers, using a Zeiss DMR 21 UV spectrometer equipped with a thermostated cell holder. A tandem cell was used. Initial concentration of the scavenger was 10^{-3} M and that of hexakis(trifluoromethylmercapto)ethane was 2×10^{-2} M. Exactly equal volumes of the benzene solutions were transferred to the tandem cell and freed from oxygen by bubbling with argon (saturated with benzene) through a capillary for 20 min. The temperature was monitored in a parallel cell. After 20 min the two solutions were mixed and registration was started ($t = 0$). The decrease of the extinction of the scavenger was registered automatically for galvinoxyl at 444 nm and for 2-phenylbis(biphenylene)allyl at 490 nm. The rate constants for dissociation of hexakis(trifluoromethylmercapto)ethane were determined from the linear parts of the experimental curves using the method described by Bartlett and Funahashi.[14,17]

Results

1. ESR Studies. At room temperature, solutions of hexakis(trifluoromethylmercapto)ethane in benzene show an ESR spectrum ($g = 2.004\ 18$) which consists of ten equally spaced lines (line width 0.35 G; intensity ratio 1:9:36:84:126:126:84:36:9:1) separated by 2.88 G which demonstrates that the radical contains nine equivalent nuclei with a spin of $^1/_2$. The spectrum is assigned to the radical $\dot{C}(SCF_3)_3$.[11] At 110 °C in liquid naphthalene the concentration of $\dot{C}(SCF_3)_3$, $a(^{19}F) = 2.96$ G, was sufficiently high to observe satellite lines from ^{13}C in natural abundance as shown in Figure 1. From the intensity pattern of these lines it is concluded that the radical contains three equivalent carbon atoms—$a(^{13}C_\gamma) = 16.04$ G—and an additional single carbon atom—$a(^{13}C_\alpha) = 40.09$ G—which supports the assignment given above. Lines from ^{33}S are not visible in the experimental spectrum, although the amplitudes of these lines are expected to be of similar magnitude as those due to $^{13}C_\alpha$. The upper limit for $a(^{33}S)$ can, however, be determined from the spectrum to be 4.5 G. This value, which would lead to overlap of the lines due to ^{33}S with those due to $^{13}C_\alpha$, $^{13}C_\gamma$, and ^{19}F, is similar to those measured[19] for $\dot{C}(SC_6H_5)_3$ and analogous radicals.

In benzene solution[15] the intensity of the lines due to $\dot{C}(SCF_3)_3$ increases reversibly with increasing temperature in the range 10-60 °C, whereas at temperatures above 70 °C the intensity of the lines decreases slowly with time indicating that some irreversible reaction occurs. The experimental results concerning the reversible formation and disappearance of $\dot{C}(SCF_3)_3$ in the temperature range up to 60 °C are rationalized in terms of homolytic fission of the C-C bond in the parent compound:

$$(CF_3S)_3C\text{—}C(SCF_3)_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2(CF_3S)_3\dot{C} \qquad (1)$$

The equilibrium constant $K = [\cdot C(SCF_3)_3{}^2]/[(CF_3S)_3CC(SCF_3)_3] = k_1/k_{-1}$ was determined by double integration of the ESR spectrum of $\dot{C}(SCF_3)_3$ and comparison with corresponding data for 10^{-5} M solutions of DPPH in benzene. At 30 °C, $K = (7.5 \pm 2.5)10^{-10}$ M, from which ΔG, the free-energy change occurring on formation of $\dot{C}(SCF_3)_3$ from $(CF_3S)_3CC(SCF_3)_3$, is calculated to be 12.6 kcal/mol. ΔH, the enthalpy change involved in reaction 1, was determined by measuring the concentration of $\dot{C}(SCF_3)_3$ as a function of temperature and plotting log $[\dot{C}(SCF_3)_3]$ vs. reciprocal absolute temperature. From the slope of the straight line which resulted from this plot $\Delta H = 13.7 \pm 0.5$ kcal/mol. The entropy change due to dissociation of $(CF_3S)_3C$-$C(SCF_3)_3$ according to reaction 1 is therefore $\Delta S = (\Delta H - \Delta G)/T = 3.6$ cal K^{-1} mol^{-1}.

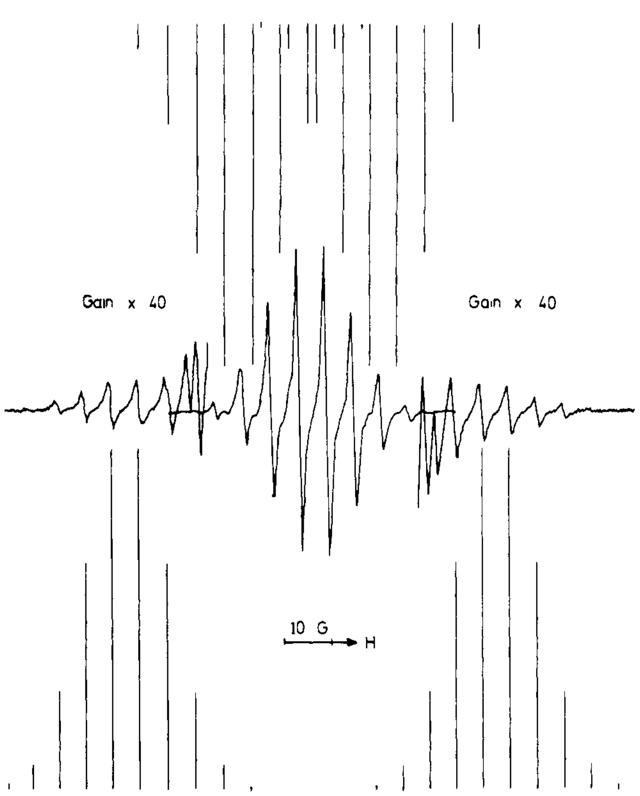

Figure 1. ESR spectrum of $(CF_3S)_3\dot{C}$ in liquid naphthalene at 110 °C. The upper and lower stick spectra indicate the positions of the satellite lines due to $^{13}C_\gamma$ and $^{13}C_\alpha$, respectively.

2. Studies on the Kinetics of Homolytic Dissociation of $(CF_3S)_3C$-$C(SCF_3)_3$. The rate constant for dissociation of $(CF_3S)C$-$C(SCF_3)_3$ was determined by scavenging $\dot{C}(SCF_3)_3$ with the stable free radicals galvinoxyl and 1-phenylbis(biphenylene)allyl. A $\geq$100-fold excess of these scavengers over that of $\dot{C}(SCF_3)_3$ (for 10^{-3} M solutions of $(CF_3S)_3CC(SCF_3)_3$ $[(CF_3S)_3\dot{C}] \approx 10^{-6}$ M) was used in order to ensure complete reaction with $\dot{C}(SCF_3)_3$. The experimental data were interpreted using the method described by Bartlett and Funahashi[14] assuming that the rate constants for reaction of $(CF_3S)_3\dot{C}$ with galvinoxyl and 1-phenylbis(biphenylene)allyl are a factor of $\geq$100 larger than that for dimerization of $(CF_3S)_3\dot{C}$, k_{-1}. The rate constants k_1 for dissociation of $(CF_3S)_3C$-$C(SCF_3)_3$ thus determined are presented in Table I. At 10-30 °C, the k_1 values are of the order 10^{-5} s^{-1} and approximately independent of the chemical nature of the scavenger used. From Arrhenius plots of the rate data $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, the activation energy and entropy for dissociation of $(CF_3S)_3C$-$C(SCF_3)_3$ are determined to be (21.0 ± 0.5) kcal/mol and (7.5 ± 2) cal K^{-1} mol^{-1}, respectively. Since the equilibrium constant *K* is known from ESR measurements, k_{-1} can be calculated. At 30 °C, $k_{-1} = 4.5 \times 10^4$ M^{-1} s^{-1}.

Discussion

With $(CF_3S)_3C$ the low value of 40.09 G for $a(^{13}C_\alpha)$, which is almost identical with corresponding values determined[19] for other methyl radicals substituted by three R-S groups, is very similar to the value of 38.5 G measured[20] for $a(^{13}C_\alpha)$ of the

Table I. Rate Constants and Activation Parameters for Dissociation of $(CF_3S)_3C\text{-}C(SCF_3)_3$

scavenger	t/°C	$k_1/10^{-5}$ s^{-1}	$H^{\ddagger}$/kcal mol^{-1}	$S^{\ddagger}$/eu
galvinoxyl	12.55	0.48	22	10
	15.30	0.73		
	20.12	1.25		
	25.01	2.71		
	29.98	4.70		
Koelsch radical	12.55	0.50	20	5
	15.25	0.66		
	20.10	1.27		
	25.05	2.15		
	30.00	4.40		

(planar) methyl radical.[21,22] In addition, the value of ≤ 4.5 G for $a(^{33}S)$ indicates that only a small fraction of the spin is delocalized onto the adjacent sulfurs. From these facts it is concluded that C_α in $(CF_3S)_3\dot{C}$ has a planar configuration. The value of 40.09 G may be compared with the value of 154.0 G determined[23,24] for $^{13}C_\alpha$ of the homologous radical $\dot{C}(OCH_3)_3$ which—according to INDO calculations—is almost perfectly pyramidal.[23]

The large coupling constant for the ^{13}C atoms in the CF_3 groups, i.e., $a(^{13}C_\gamma) = 16.04$ G as compared to 7.5 G for $a(^{13}C_\gamma)$ in the radical $\dot{C}(SC_6H_5)_3$,[19] does not necessarily indicate that the unpaired spin is delocalized, since with $CF_3CH_2\dot{C}(CMe_3)_2$, in which the spin is localized, the coupling constant for the ^{13}C atom in the CF_3 group is even larger (30.1 G).[25]

Preliminary results of an X-ray investigation[26] and an electron diffraction study[27] of the structure of $(CF_3S)_3C\text{-}C(SCF_3)_3$ indicate that (a) the central carbon atoms in this molecule have essentially a planar configuration and (b) the C-C bond distance (1.7 Å as compared to 1.54 Å in ethane) is anomalously large. Both effects are suggested to be due to the strong steric interaction of the six CF_3S groups (F- and B-strain),[28-31] which results in converting the tetrahedral configuration of the carbons into one approximating a planar structure. The ground state of $(CF_3S)_3C\text{-}C(SCF_3)_3$ must therefore be quite similar to the transition state for the homolytic bond cleavage reaction 1. This interpretation is supported by the low value of $\Delta S^{\ddagger}$ (7.5 cal K^{-1} mol^{-1}), which is only 50% of that observed for homolytic fission of ethane (17.2 cal K^{-1} mol^{-1})[32] and which demonstrates that the difference in the degree or kind of order between ground and transition state is unusually low.

From the activation energy for C-C bond dissociation ($\Delta H^{\ddagger} = 21.0$ kcal/mol) and the C-C bond energy ($\Delta H = 13.7$ kcal/mol) the activation energy for dimerization of $\dot{C}(SCF_3)_3$, the rate of which ($k_{-1} = 10^4$ M^{-1} s^{-1}) is much lower than diffusion controlled, is calculated as 7.3 kcal/mol. This value leads to a preexponential factor of 10^9–10^{10} M^{-1} s^{-1} for the dimerization reaction reverse (1). The low value for the rate constant for dimerization of $(CF_3S)_3\dot{C}$ is reasonable in view of the strong steric interaction (F- and B-strain) of the CF_3S groups in the transition state. In conclusion it is suggested that the radical $\dot{C}(SCF_3)_3$ is not a stable but a "persistent"[33] radical and that the unusually low[34] C-C bond dissociation energy is not the result of a stabilization of the radicals formed but is caused by sterically induced destabilization of the parent compound.

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