the lifetime of the $C_6F_{14}^-$ ion, under collision-free conditions, is at least 1 μsec.

The results presented here would thus strongly suggest the decrease in radiolytical hydrogen yield in the solution of cyclic perfluorocarbons in alkanes is due to electron scavenging by these solutes. The subsequent neutralization reaction between the solvent positive ion and the solute anion would be expected to result in smaller yields of radiolytical products.[15] The main difference between the electron-scavenging abiltiy of the perfluorocyclocarbons and the alkyl and benzyl halogenated compounds would thus lie in the fact that in the case of the former electron attachment is nondissociative, whereas in the latter electron capture has been observed only in the cases where the electron affinity of the halogen atom exceeds the bond dissociation energy of the carbon–halogen bond[2,3,16] and conditions are favorable for the occurrence of a dissociative process. The nondissociative electron attachment of the perfluoro compounds results from the fact that the C–F bond strength exceeds the electron affinity of the fluorine atom. In their ability to accommodate an external electron, the perfluorocyclic compounds would thus seem to be comparable to polynuclear aromatic molecules, several of which, such as naphthalene, naphthacene, pyrene, etc., are known to attach thermal electrons in the gas phase.[17] The comparison of the K_{N_2O} values obtained for anthracene and pyrene, 0.6 and 0.5, respectively,[12] with those obtained for perfluorocyclocarbons would suggest a higher stability of the perfluorinated anions.

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The Reactions of Selenium Atoms. I. Addition and Insertion Reactions of Selenium (4^1D_2) Atoms with Olefins and Paraffins

Sir:

Reactions of selenium atoms with olefins have been reported by Callear and Tyerman.[1] In flash-photolyzed CSe–olefin mixtures, transient spectra were observed and tentatively assigned to episelenides. From the time dependence of the spectral intensities it was possible to obtain absolute rate constants for a series of olefins. Preliminary experiments were also performed with COSe, and it was concluded that selenium atoms in the 4^1D_2 state were formed by photolysis of COSe in analogy with COS.[2]

Recently in this laboratory a mass spectrometric technique has been developed[3] for the time-resolved detection of transient intermediates in flash-photolyzed systems. Detection does not depend on the electronic absorption characteristic of the transient, and, in combination with kinetic absorption spectroscopy, the technique assumes great flexibility.

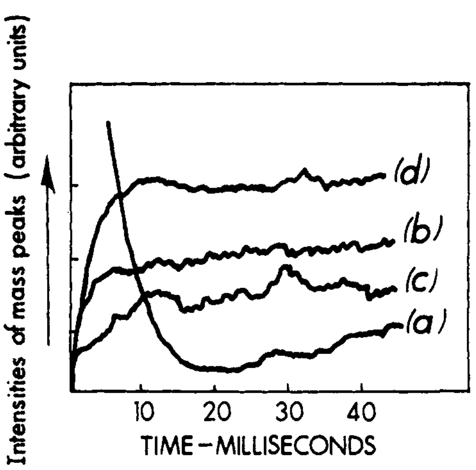

Figure 1. Variation with time of intensities of mass peaks, from oscillograms: (a) decay of Se_2 (*m/e* 160) (full scale 2 v); (b) formation of propyl selenomercaptan (*m/e* 124) (full scale 500 mv); (c) formation of HSe (*m/e* 81) as a fragment of propyl selenomercaptan (full scale 200 mv); (d) formation of an adduct in flashed C_2D_4–COSe with *m/e* 112 (full scale 1 v).

Our apparatus consists, in essence, of a photolysis cell attached to a small leak into the ion source of an Atlas CH_4 mass spectrometer. Selected mass peaks can be studied with a response time of a few milliseconds, and thereafter at times limited by bleeding of the photolyzed mixture into the ion chamber. Typical photolytic flash energies were $\sim$2000 joules, passed into a reaction volume of $\sim$5 ml. A full description of the equipment will appear elsewhere.[3]

Three aspects of selenium atom chemistry were explored: polymerization, insertion into C–H and C–D bonds of paraffins, and addition to olefinic double bonds. Reaction mixtures contained 20 μ of COSe and 300 μ of other reagents and 15 torr of He. Approximately 10% of the COSe was decomposed per flash.

Figure 1(a) shows the rapid production and decay of Se_2 (*m/e* 160); the apparent increase at longer delays is ascribed to the cracking patterns of higher polymers. When $\sim$3 torr of CO_2 was present in the reaction mixture, the Se_2 yield was much decreased, indicating that (like $S(3^1D_2)$) $Se(4^1D_2)$ is deactivated by CO_2 and that the abstraction

$$Se(4^1D_2) + COSe \longrightarrow CO + Se_2 \qquad (1)$$

is more rapid than the analogous reaction of $Se(4^3P)$. Se_3 was not detected in COSe–He mixtures after flashing, which is further indication that the atoms are rapidly consumed by (1).

Experiments with propane, cyclopropane, cyclobutane, ethane, methylsilane, isobutane, etc., demonstrated insertion of excited selenium atoms into C–H and possibly Si–H bonds. Figures 1(b) and 1(c) show formation of propyl selenomercaptan (*m/e* 124) and the corresponding fragment, HSe^{80} (*m/e* 81). For the first three hydrocarbons cited above, the HSe peak was about 10% as intense as those of the parent adducts, indicating that selenomercaptans are major products. Se_2 formation was not suppressed, even though 15-fold excesses of the hydrocarbons were present, showing either that insertion is less rapid than (1), or that

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[1] A. B. Callear and W. J. R. Tyerman, *Proc. Chem. Soc.*, 296 (1964); *Trans Faraday Soc.*, **61**, 2395 (1965); *ibid.*, **62**, 371 (1966).

[2] I. G. Csizmadia, K. S. Sidhu, O. P. Strausz, and H. E. Gunning, *J. Am. Chem. Soc.*, **88**, 2412 (1966).

[3] W. K. Duholke, R. Messmer, P. Kebarle, O. P. Strausz, and H. E. Gunning, to be published.

$Se(4^1D_2)$ atoms, like $S(3^1D_2)$ atoms,[4] suffer deactivation parallel to insertion. Final confirmation of our assignment comes from the experiments with C_3D_8; in addition to the adduct peak (*m/e* 132), a second peak formed slowly at *m/e* 131. This shows that the adduct contains a labile deuterium atom which is exchanged for H from the walls of the reaction system. No hexane was formed in flashed COSe–C_3H_8 mixtures, indicating that selenomercaptan formation is a single-stage process; if abstraction of H occurred and was followed by combination of HSe and C_3H_7, we would expect some C_6H_{14} also to be formed.

Figure 1(d) shows formation and decay of an adduct in flashed C_2D_4–COSe, which is likely the episelenide, since no labile D atom was present (*cf.* C_3D_8Se, above) and the cracking pattern from C_2H_4Se contained no CH_3^+. The apparent absence of a C–D insertion product is an interesting distinction from $S(3^1D_2)$ which yields about equal quantities of vinylthiol and thiacyclopropane with ethylene.[4] The episelenides from a series of substituted olefins (C_2F_4, $SiH_3CH{=}CH_2$, $CF_3CH_3C{=}CH_2$, $CHCl{=}CHCl$, etc.) have also been detected. All are inherently unstable at room temperature and decay with half-lives between 30 msec and a few seconds. Decomposition of the episelenide, if it occurs in the gas phase, is probably bimolecular, giving Se_2 and two olefin molecules, or by reaction with COSe.[5] When the episelenide was trapped at 77°K in a fast flow system, an oil was observed on rewarming to room temperature which we were unable to characterize by conventional methods. The mass spectrometric detection of episelenides confirms the spectral assignment of Callear and Tyerman.[1] Some of these reactions may have synthetic value; cyclopropyl and cyclobutyl selenomercaptans have not been reported previously.

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[5] Homogeneous, unimolecular decomposition would lead to the equilibrium

$$\mathrm{Se} + \mathrm{C{=}C} \rightleftharpoons \overline{\mathrm{Se}}$$

which would be contradictory to the excellent rate data reported in ref 1.

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Carbon Monoxide Reactions. I. A Novel Synthesis of Acid Chlorides

Sir:

We wish to report a novel reaction which converts saturated compounds into carboxylic acid chlorides by the substitution of a chloroformyl group (COCl) for hydrogen.

The formation of acyl radical from alkyl radical and carbon monoxide ($R\cdot + CO \rightleftharpoons RCO\cdot$) has been demonstrated in the copolymerization of ethylene and CO and in the desulfurization of thiyl radical in the presence of CO,[1] while the conversion of acyl radicals to acid chlorides ($RCO\cdot$ + halogen donor $\rightarrow$ RCOX) occurs in the free-radical chlorination of aldehydes.[2] We reasoned that it might be possible to affect the carbonylation of alkyl radicals in the presence of a radical halogenating reagent such that acid halide would be produced in preference to alkyl halide. The following chain-propagating steps (initiation and terminations not shown) were envisioned

$$RH + Y\cdot \longrightarrow R\cdot + HY \tag{1}$$

$$R\cdot + XY \longrightarrow RX + Y\cdot \tag{2}$$

$$R\cdot + CO \rightleftharpoons RCO\cdot \tag{3}$$

$$RCO\cdot + XY \longrightarrow RCOX + Y\cdot \tag{4}$$

where X represents halogen and Y a chain-carrying species such as Cl, Br, CCl_3, Cl_3CS, etc. The sequence of steps 1, 3, and 4 would give acid halide, while step 1 followed by 2 would produce the undesired alkyl halide.

Experiments using either chlorine, bromine, *t*-butyl hypochlorite, trichloromethanesulfonyl chloride, trichloromethanesulfenyl chloride, or sulfuryl chloride with cyclohexane and CO (6000 psi at 25°) together with *t*-butyl peroxide, at 130° for about 16 hr, gave exclusively halocyclohexane. Both vpc and infrared were unable to detect even traces of acid halide or the corresponding ester after treatment with ethanol.

It became apparent that a reagent which transfers a halogen atom more slowly was required if the reaction of alkyl radical with carbon monoxide was to complete effectively against the reaction of alkyl radical with the halogenating agent. Some polyhalohydrocarbons will effectively halogenate paraffins[3] and many transfer halogen to alkyl radical, formed, for example, by radical addition to an olefin, so slowly that olefin telomerization is a competing reaction.[4] Since the rates of addition of alkyl radical to carbon monoxide and to ethylene are competitive,[5] we reasoned that the addition of alkyl radical to carbon monoxide should be competitive with the transfer of a halogen to the alkyl radical by the polyhalohydrocarbon.

Initial experiments with a peroxide-initiated reaction of a 2:1 (molar ratio) solution of cyclohexane and carbon tetrachloride with 6000 psi of CO in a rocked chrome–vanadium steel Aminco microbomb at 130° for 16 hr produced for the first time cyclohexanecarboxylic acid chloride as the major reaction product along with lesser quantities of chlorocyclohexane. The conversions, however, were very low; less than 10% of the CCl_4 had undergone reaction. Not only was the conversion to acid chloride very low, but the simple chlorination of cyclohexane by the CCl_4, which went to completion under the same conditions in the absence of CO, was also strongly retarded. The chlorocarbonylation (5) and the competing chlorination (6) are apparently both retarded, and since they have several inter-

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[1] (a) M. M. Brubaker, D. D. Coffman, and H. H. Hoehn, *J. Am. Chem. Soc.*, 74, 1509 (1952); (b) C. Walling, O. H. Basedow, and E. S. Savas, *ibid.*, 82, 2181 (1960).

[2] (a) S. Winstein and F. H. Seubold, Jr., *ibid.*, 69, 2916 (1947); (b) D. Ginsburg, *ibid.*, 73, 702 (1951).

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[5] D. D. Coffman, P. S. Pinkney, F. T. Wall, W. H. Wood, and H. S. Young, *J. Am. Chem. Soc.*, 74, 3391 (1952).