$Se(4^1D_2)$ 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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[4] H. E. Gunning and O. P. Strausz, *Advan. Photochem.*, **4**, 143 (1966).

[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

$$RH + Y\cdot \longrightarrow R\cdot + HY \qquad (1)$$

$$R\cdot + XY \longrightarrow RX + Y\cdot \qquad (2)$$

$$R\cdot + CO \rightleftharpoons RCO\cdot \qquad (3)$$

$$RCO\cdot + XY \longrightarrow RCOX + Y\cdot \qquad (4)$$

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).

[3] J. P. West and L. Schmerling, *ibid.*, **72**, 3525 (1950).

[4] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp 247–265.

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

mediate chain-propagating steps in common, the chlorination reaction (6) was used as a model to determine the source and nature of the retardation.

$$\mathrm{RH} + \mathrm{CCl_4} + \mathrm{CO} \longrightarrow \mathrm{RCOCl} + \mathrm{CHCl_3} \qquad (5)$$

$$\mathrm{RH} + \mathrm{CCl_4} \longrightarrow \mathrm{RCl} + \mathrm{CHCl_3} \qquad (6)$$

A series of peroxide-initiated chlorinations was carried out using $CCl_4$ and cyclohexane in glass tubes containing different added materials (Table I). Filings from the metal pressure reactor had no effect on the chlorination reaction (6), while 10% acid chloride had a modest influence; however, the combination of 10% acid chloride and a trace of metal (two sandlike grains) produced a significant decrease in conversion, while acid chloride along with 3% of the chrome–vanadium steel caused a dramatic decrease in conversion. The combination of acid chloride and steel appeared to act in concert, either producing a radical-chain inhibitor or destroying the peroxide initiator.

**Table I.** The Influence of Metal and Acid Chloride on the Chlorination of Cyclohexane by Carbon Tetrachloride

| Conversion,[a] % | Acid chloride added,[b] % | Metal added,[b] % |
|---|---|---|
| 95 | None | None |
| 93 | None | 3 |
| 85 | 10 | None |
| 40 | 10 | Trace |
| 8 | 10 | 3 |

[a] $CCl_4$ converted to chlorocyclohexane and $CHCl_3$. [b] Per cent of initial $CCl_4$.

A tube within a tube glass liner designed to minimize contact (by transfer of liquid through the CO weep holes in the liner by means of the rocking motion of the reactor) of the liquid reactants with the metal reactor was used in subsequent reactions. Good reproducible selectivities to acid chloride of up to 84% were obtained using this liner, while conversions, although quite acceptable, were subject to variation (Table II). We suspect that transfer of variable trace quantities of contaminant, from acid chloride–metal interaction, back into the liner caused the variation in conversions during the fixed reaction interval.

**Table II.** Peroxide-Initiated Chlorocarbonylation of Cyclohexane Using a Concentric Tubular Glass Reactor Insert[a]

| CO pressure, psi at 25° | Conversion[b] after 16 hr, % | Selectivity to acid chloride, % |
|---|---|---|
| 8000 | 34–49 | 89 ± 0.2[c] |
| 6000 | 44–46 | 84 ± 0.5 |
| 4000 | 27–41 | 74 ± 1.0 |
| 2000 | 42–55 | 56 ± 1.0 |
| 1000 | 45–72 | 38 ± 2.7 |

[a] Cyclohexane:$CCl_4$ 2:1; 5% *t*-butyl peroxide; 130°. [b] Based on initial $CCl_4$ concentration, for 16-hr runs. [c] Chlorocyclohexane 11%.

The ratio of acid chloride to alkyl chloride is plotted in Figure 1 as a function of the carbon monoxide pressure. The increasing slope indicates that this ratio is proportional to about the 1.3 power of the CO pressure. The 0.3 power may represent the deviation of CO concentration dependence on pressure from Henry's law.

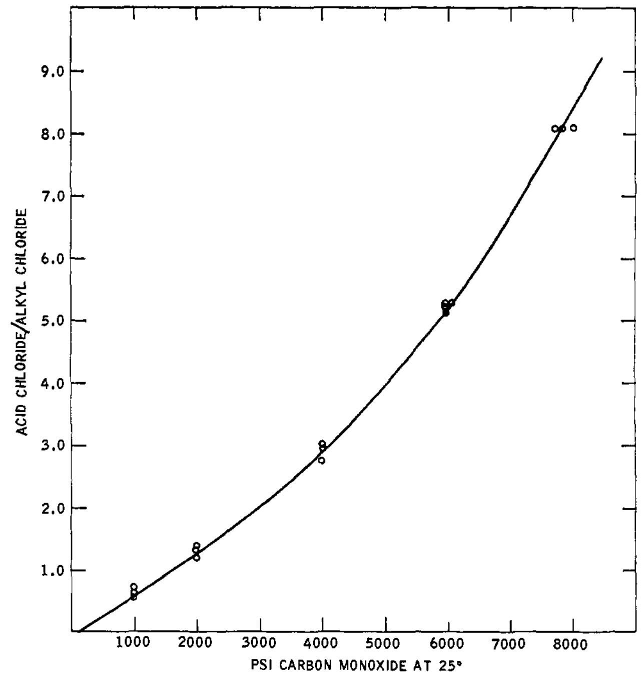

Figure 1. Effect of CO pressure on the ratio of acid chloride to alkyl chloride.

The scope and mechanism of the chlorocarbonylation of a variety of paraffins with $CCl_4$ and CO is presently being investigated.

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## Separation of Conformers.
## I. Axial and Equatorial Isomers of Monosubstituted Cyclohexanes

*Sir:*

The possibility of separating axial and equatorial isomers or boat forms of monosubstituted cyclohexanes has aroused the curiosity of chemists ever since the existence of different conformations in the molecules was postulated.[1] Claims of the isolation of conformational isomers of monosubstituted cyclohexyl compounds (stable at room temperature) have been made,[2] but the validity of these reports has been effectively challenged.[3] Now that data for the energy barriers of the chair–chair[1] interconversion of cyclohexane[4] and derivatives are

(1) H. Sachse, *Ber.*, **23**, 1368 (1890); *Z. Physik. Chem.*, **10**, 203 (1892); E. Mohr, *J. Prakt. Chem.*, **98**, 315 (1918); C. W. Becket, K. S. Pitzer, and R. Spitzer, *J. Am. Chem. Soc.*, **69**, 977, 2488 (1947).

(2) Examples are found in: (a) M. Quadrat-I-Kuda, *J. Indian Chem. Soc.*, **8**, 277 (1931); (b) D. M. Cowan, G. H. Jeffrey, and A. I. Vogel, *J. Chem. Soc.*, 1862 (1939).

(3) S. Goldschmidt and G. Grafinger, *Ber.*, **68**, 279 (1939); R. F. Miller and R. Adams, *J. Am. Chem. Soc.*, **58**, 787 (1936).

(4) F. R. Jensen, D. S. Noyce, C. H. Sederholm, and A. J. Berlin, *ibid.*, **84**, 386 (1962).