HYDROCARBON OXIDATIONS WITH
CHROMYL TRIFLUOROACETATE

J. William Suggs[*] and Larry Ytuarte
Department of Chemistry, Brown University
Providence, RI 02912

Abstract. Chromyl trifluoroacetate oxidizes hydrocarbons, including polyolefin polymers, to give predominately alcohols and ketones. The reaction is extremely rapid. A solution of n-hexane, for example, is oxidized upon mixing at $-50°$.

The ability of ligands to modulate the reactivity of a metal center is exhibited most strongly in the chemistry of Cr(VI). At one end of the reactivity scale are reagents such as $(C_5H_5N)_2CrO_3$, PCC and PDC which oxidize polyfunctional organic molecules selectively and efficiently.[1] At the other end of the reactivity scale is the topic of this letter, chromyl trifluoroacetate.

As described by Gard and coworkers, $CrO_2(O_2CCF_3)_2$ is prepared from CrO_3 and $(CF_3CO)_2O$.[2] It is a yellow-brown, hygroscopic solid which is decomposed by moisture. It can be stored for several weeks in the dark without loss of activity. The solvents one can use with it are limited by its reactivity. CH_2Cl_2, for example, reacts upon mixing. However, halocarbon solvents without C-H bonds such as CCl_4 and $F_2ClCCFCl_2$ were compatible with $CrO_2(O_2CCF_3)_2$.

Results of the reactions of various hydrocarbons with chromyl trifluoroacetate are given in the table. Oxidations were performed by adding 0.5 mmol of hydrocarbon in 5 ml of CCl_4 to 2 mmol of $CrO_2(O_2CCF_3)_2$ in 40 ml of CCl_4. This mole ratio was chosen since it resulted in the complete reaction of adamantane. In all cases the solution turned black upon mixing and a gummy solid precipitated. After 30 min excess 0.1 M $NaHSO_3$ was added. The organic layer was analyzed for products by gc. The table lists all products formed in greater than 0.5% yield. To increase the material balance, the green aqueous layer was heated at reflux with 10 ml of CH_3OH for 2 hr and extracted with CCl_4, but this had only a minor effect on product yields. As is the case with other strong oxidants, the material balance in these reactions was low.[3] One of the procedures we tried in order to recover more product involved, in the adamantane reaction, removal of the solvent by distillation followed by reflux of the black residue with $LiAlH_4$ in THF. No additional amounts of products were detected.

As can be seen from the table, $CrO_2(O_2CCF_3)_2$ is an exceptionally powerful oxidant, reacting within seconds even with n-hexane at $-50°$. There is a preference for oxidation at sites that can stabilize positive change (or a radical), which is seen for other Cr(VI) reagents.[4] The only hydrocarbon that did not react with $CrO_2(O_2CCF_3)_2$ was methane, which is consistent with

Table   Oxidation of Hydrocarbons with $CrO_2(O_2CCF_3)_2$

| Substrate[a]			Products (%)[b]	
1. Adamantane		Adamantane	1-Adamantanol	1-Adamantyl trifluoroacetate
mole ratio Cr(VI)/RH	1:1	68	22	2.3
	4:1	0	27	4.0
2. Toluene	Toluene	Benzaldehyde	Benzyl Trifluoroacetate	Benzoic acid
25°	0	16	7.5	4.2
-20°	0	19	8.7	3.6
3. Cyclohexane		Cyclohexane	Cyclohexanone	Cyclohexyl Trifluoroacetate
		14	15	0.8
4. n-Hexane		n-Hexane	2-Hexanone	3-Hexanone
25°		27	10	7.5
-50° [c]		28	9	6
5. Deoxybenzoin		Deoxybenzoin	Benzil	Benzoic acid
		0	3	4
6. Benzil		Benzil	Benzoic acid	
		0	20	
7. Ethylbenzene		Ethylbenzene	Acetophenone	
		0	51	
8. Norbornane		Norbornane	Norcamphor	exo-2-Norbornyl trifluoroacetate
		19	14	4
9. Indan		Indan	1-Indanone	1-Indanyl-3-trifluoroacetate
		0	23	7

a) mole ratio of oxidant to product was 4:1, temperature was 25°, unless other-
wise noted

b) Product yields were determined by gc on 10m OV101 capillary column using
n-decane as an internal standard. Products were identified by comparison of
their mass spectra and gc retention times with authentic samples.

c) Solvent: 1:1 (v:v) CCl_4: F_3CCCl_3

a high degree of carbocation character in the oxidation transition state. There are at least two reasons for the need for excess reagent in these oxidations. First, tertiary alcohols exchange with $CrO_2(O_2CCF_3)_2$ forming $CrO_2(OR)_2$ and CF_3CO_2H. The latter Cr(VI) species are not particularly powerful oxidants. Second, the chromium tars formed in these oxidations inhibit oxidation. Addition of a CCl_4-washed sample of the Cr residue to an adamantane-$CrO_2(O_2CCF_3)_2$ reaction inhibited hydrocarbon oxidation.

Calculations have recently supported the occurrence of a Cr-R intermediate in Cr(VI) oxidations

$$RH \quad + \quad CrO_2X_2 \quad \longrightarrow \quad \begin{array}{c} HO \diagdown \diagup R \\ X-Cr-X \\ \| \\ O \end{array}$$
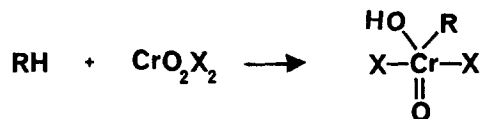
of hydrocarbons.[5] Such a species could undergo either reductive elimination to ROH or $ROCOCF_3$ or homolysis to give an alkyl radical and a Cr(V) intermediate. We have evidence for a Cr(V) compound being formed during these oxidations, although we cannot yet say by what mechanism it arises. When an esr tube with a frozen CCl_4 solution of $CrO_2(O_2CCF_3)_2$ below a frozen adamantane solution is allowed to warm in the esr cavity, at $-23°$ a strong signal with g=1.970 grows in[6,7]. By the time $25°$ is reached (15 min) the signal has virtually disappeared. This signal arises from a Cr(V) species since we see hyperfine coupling to ^{53}Cr(9.5%), and the g value is in the range of other Cr(V) species.

Chromate oxidation of polyolefins have been used commercially to improve the adhesion properties of the polymer surface.[8,9] As predicted from the results of the oxidation of simple hydrocarbons, $CrO_2(O_2CCF_3)_2$ can functionalize polyethylene surfaces also. Powdered polyethylene (Aldrich, spectroscopic grade) was oxidized at $25°$ with $CrO_2(O_2CCF_3)_2$, followed by water washes and vacuum drying of the powder. A transmission ir of a film pressed from the oxidized powder is shown below. New bands due to C-O single and double bands are evident, as well as some remaining Cr=O species. A blank ir showed only hydrocarbon bands.

440

REFERENCES

1. Cainelli, G.; Cardillo, G. "Chromium Oxidations in Organic Chemistry", Springer-Verlag, Berlin 1984.

2. Gard, G. L.; Gerlach, J. N. Inorg. Chem. 1970, 9, 1565.

3. Enqvist, J. Ann. Acad. Sci. Fennicare Ser. A Chemica 1977, 183, 1.

4. Wiberg, K. B. "Oxidation in Organic Chemistry" Part A, Academic Press, New York, 1965, p.69.

5. Rappe, A. K.; Goddard, W. A., III J. Am. Chem. Soc. 1982, 104, 3287.

6. Wiberg, K. B.; Lepse, P. A. J. Am. Chem. Soc. 1964, 86, 2612.

7. Miyaura, N.; Kochi, J. K. J. Am. Chem. Soc. 1983, 105, 2368.

8. Wu, S. "Polymer Interface and Adhesion" Marcel Dekker, New York, 1982, pp.284-291.

9. Nuzzo, R. G.; Smolinsky, G. Macromolecules 1984, 17, 1013.