collected from the reaction mixture showed the presence of CO_2, propene, and CO. The concentration of CO_2 corresponded to a molar amount approximately equal to the total amount of **1** and **2** isolated. The concentration of propene was about 2.2 times as great as that of CO_2.

One gram of the mixture of **1** and **2** was dissolved in pentane and hydrogenated with 0.5 g of 5% Pd on carbon catalyst for 2 hr at 50° and 40 psi hydrogen pressure. Pure **2** (0.73 g) was isolated and no **1** was present. *Anal.* Calcd for $C_{13}H_7Co_3O_9$, **2**: C, 32.23; H, 1.46. Found: C, 31.94; H, 1.32.[7]

The nmr spectra were determined with a Varian Associates Model A-60D spectrometer. Infrared spectra were obtained with a Perkin-Elmer Model 621 spectrophotometer. Mass spectra were obtained on a Consolidated Electrodynamics Corp. Model 21-110B spectrometer and a Finnigan Model 1015 S/L gas chromatograph mass spectrometer.

Results and Discussion

The reaction of dimethylketene with $Co_2(CO)_8$ under the conditions described in the Experimental Section is slower than the thermal dimerization of dimethylketene. Thus, the major product is tetramethyl-1,3-cyclobutanedione. However, significant amounts of CO_2, propene, μ_3-(isopropenylmethylidyne)-*cyclo*-tris(tricarbonylcobalt)(3 *Co–Co*) (**1**), and μ_3-(isopropylmethylidyne)-*cyclo*-tris(tricarbonylcobalt)(3 *Co–Co*) (**2**) are isolated from decarbonylation and deoxygenation of dimethylketene.

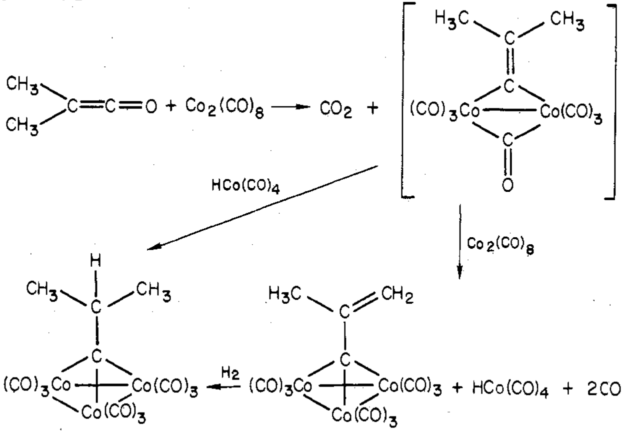
We believe that the formation of **1** results from the reaction of a second mole of $Co_2(CO)_8$ with a cobalt-coordinated dimethylvinylidene intermediate. Closure of the methylidynetricobalt cluster could be accompanied by the transfer of hydride from a methyl group of the intermediate; $HCo(CO)_4$ and a carbon–carbon double bond would then result. Tetracarbonylhydrocobalt could then either liberate hydrogen, which would reduce some **1** to **2**, or add directly to the dimethylvinylidene intermediate, which would produce **2** and release 2 mol of CO. The hydrogenation of **1** to **2** was accomplished with palladium on carbon catalysts under relatively mild conditions. (See Scheme I.)

We believe that propene is formed in a side reaction in which $Co_2(CO)_8$ decarbonylates dimethylketene. A metal-coordinated isopropylidene intermediate is probably formed. An analogous intermediate was proposed[1] for the formation of tetraphenylethylene from diphenylketene. Propene must be released at a rate appreciably faster than the rate of dimerization to the analogous tetramethylethylene. The presence of small quantities of tetramethylethylene and 2,3-dimethylbutane in the reaction mixture was verified by gas chromatographic mass spectral analysis.

Rupilius and Orchin[8] recently proposed a mechanism whereby tetracarbonylisobutyrylcobalt may disproportionate and produce both propene and isobutyraldehyde. The possibility exists that $HCo(CO)_4$ could add directly to dimethylketene and produce tetracarbonylisobutyrylcobalt. However, gas chromatographic–mass spectral examinations of the reaction mixture, prior to the admission of air, failed to show the presence of even traces of isobutyraldehyde, butyraldehyde, isobutyric acid, or butyric acid. We therefore conclude that this is not the mechanism by which propene is formed.

An attempt to trap a dimethylvinylidene-bridged intermediate by the substitution of $Co_2(CO)_6[(C_6H_5)_3P]_2$ for $Co_2(CO)_8$ led to the quantitative formation of the reported[9] polyester **3** $[-OC[=C(CH_3)_2]C(CH_3)_2CO-]_n$. The reaction of excess dimethylketene with $Rh[(C_6H_5)_3P]_3Cl$ gave the following products: $RhCO[(C_6H_5)_3P]_3Cl$, **3**, the β-lactone dimer of dimethylketene (3-hydroxy-2,2,4-trimethyl-3-pentenoic acid, β-lactone),[10] and small amounts of both tetramethylethylene and 2,3-dimethylbutane. The polyester **3** was also obtained quantitatively from the reaction of dimethylketene with catalytic amounts of both $Fe(CO)_5$ and $Fe_2(CO)_9$.

Scheme I



The interesting chemistry of dimethylketene and related heterocumulenes with organometallic substrates is being investigated further.

Registry No. μ_3-(Isopropenylmethylidyne)-*cyclo*-tris(tricarbonylcobalt)(3 *Co–Co*), 36974-38-6; μ_3-(isopropylmethylidyne)-*cyclo*-tris(tricarbonylcobalt)(3 *Co–Co*), 33937-52-9; $RhCO[(C_6H_5)_3P]_3Cl$, 28912-94-9.

Acknowledgment. I wish to thank Drs. Hans K. Dietl and Kent C. Brannock for their assistance through valuable discussions.

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[7] Compound **2** was reported from the reaction of $CCl_3C(CH_3)_2OH$ with $Co(CO)_4^-$: G. Palyi, F. Piacenti, M. Bianchi, and E. Benedetti, *Acta Chim. Acad. Sci. Hung.*, **66**, 127 (1970). For a recent review of $Co_3(CO)_9CY$ compounds see G. Palyi, F. Piacenti, and L. Marko, *Inorg. Chim. Acta Rev.*, **4**, 109 (1970).

[8] W. Rupilius and M. Orchin, *J. Org. Chem.*, **37**, 936 (1972).

[9] G. Natta, G. Mazzanti, G. Pregaglia, M. Binaghi, and M. Peraldo, *J. Amer. Chem. Soc.*, **82**, 4742 (1960).

[10] R. H. Hasek, R. D. Clark, E. U. Elam, and J. C. Martin, *J. Org. Chem.*, **27**, 60 (1961).

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Chemistry of Chromyl Fluoride. II.[1] A New and Useful Preparation of Chromyl Nitrate[2]

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Chromyl nitrate $[CrO_2(NO_3)_2]$ was probably first prepared by Schmiesser and Lutzow in 1954,[4] by the reaction of CrO_2Cl_2, $KClCrO_3$, or CrO_3 with N_2O_5. In our studies of CrO_2F_2 we have found a new and versatile method of preparing $CrO_2(NO_3)_2$ that does not require the preparation and handling of N_2O_5. When $NaNO_3$ is treated with excess CrO_2F_2, chromyl

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[1] Part I: W. V. Rochat, J. N. Gerlach, and G. L. Gard, *Inorg. Chem.*, **9**, 998 (1970).

[2] Presented at the 27th Regional Meeting of the American Chemical Society, Corvallis, Ore.

[3] PRF Undergraduate Scholar.

[4] M. Schmiesser and D. Lutzow, *Z. Angew. Chem.*, **66**, 230 (1954).

nitrate is produced in yield greater than 90% according to the equation

$$2NaNO_3(s) + 2CrO_2F_2(g) = CrO_2(NO_3)_2 + Na_2CrO_2F_4(s) \quad (1)$$

Depending upon the temperature, varying amounts of O_2 and $CrO_2(NO_3)_2$ are produced. When reaction 1 proceeds at 55-60° for 5 days a yield of only 40% $CrO_2(NO_3)_2$ with large amounts of O_2 is produced but at room temperature for 12 days the yield of $CrO_2(NO_3)_2$ is increased to over 90% with a small amount of O_2. The chromyl nitrate produced in this reaction is essentially pure and free of any NO_2 produced from its decomposition. When $CrO_2(NO_3)_2$ decomposes, the following reaction scheme is thought to occur[5]

$$CrO_2(NO_3)_2 = CrO_3(s) + N_2O_5(g) \quad (2)$$

$$N_2O_5(g) = N_2O_4(g) + {}^1\!/_2O_2(g) \quad (3)$$

$$N_2O_4(g) = 2NO_2(g) \quad (4)$$

The absence of NO_2 which should have been formed along with O_2 from the decomposition of $CrO_2(NO_3)_2$ produced in reaction 1 is explained by the reaction in which the NO_2 reacts with any excess chromyl fluoride

$$2NO_2(g) + CrO_2F_2(g) = (NO_2)_2{\cdot}CrO_2F_2(s) \quad (5)$$

The structure of this nonvolatile greenish solid product has not been elucidated but it is clear that the chromium is in a reduced state (this is probably the first example of an inorganic Etard complex). The $Na_2CrO_2F_4$ produced along with $CrO_2(NO_3)_2$ in reaction 1 has also been prepared by allowing NaF to react directly with CrO_2F_2 according to

$$2NaF(s) + CrO_2F_2(g) = Na_2CrO_2F_4(s) \quad (6)$$

The formation of $Na_2CrO_2F_4$ suggested the possibility of a similar complex being formed with $NaNO_3$. We have isolated such a complex from the reaction of CrO_2F_2 with excess $NaNO_3$ in the presence of a solvent (perfluoroheptane) (eq 7).

$$2NaNO_3(s) + CrO_2F_2(g) \overset{C_7F_{16}}{=} Na_2CrO_2F_2(NO_3)_2(s) \quad (7)$$

When this complex is quickly heated, decomposition to $CrO_2(NO_3)_2$, O_2, NO_2, CrO_3, and NaF occurs around 90°. With excess $NaNO_3$ and in the absence of the solvent very little $CrO_2(NO_3)_2$ or the complex $Na_2CrO_2F_2(NO_3)_2$ was formed.

Experimental Section

Chemicals and Equipment. Chromyl fluoride was prepared essentially by the method of Flesch and Svec.[6] The infrared spectrum agreed with the literature.[7] Any HF present was removed by contacting the CrO_2F_2 with dried NaF. The $NaNO_3$ used was of analytical reagent purity (Mallinckrodt) and was dried at 110° for 1 hr prior to use. NaF was of analytical reagent purity (Mallinckrodt) and was dried in a nickel crucible at red heat for 45 min and placed in a desiccator to cool. Matheson's NO_2 was used as received.

The infrared spectra were recorded on a Perkin-Elmer 137 Infracord spectrophotometer. The infrared cell (NaCl windows) used for gases was made of Monel metal and equipped with a Whitney brass valve. The path length of the cell was 8.25 cm. The infrared spectra of solid compounds and $CrO_2(NO_3)_2$[8] were taken neat between NaCl plates. All spectra were calibrated with polystyrene. The ultraviolet spectrum of $CrO_2(NO_3)_2$ was recorded using a Cary Model 14 recording ultraviolet spectrophotometer. The liquid spectrum was taken with a cell having a path length of 1.00 cm. The CCl_4 used in this work was of gas chromatographic spectrophotometric quality (Mallinckrodt "Spectrar").

X-Ray powder spectra were obtained for the solids contained in 0.5-mm Lindemann glass tubes. Exposure of 2-4 hr was made using XRD-5 GE camera. Nickel-filtered copper radiation (Cu Kα radiation) was used. Our procedure was standardized using known compounds in which the calculated *d* values agreed with the published ASTM values.

Chemical Analyses. The chromium content was determined iodometrically, after hydrolysis, by quantitatively reducing chromic acid to trivalent chromium. The acidity was determined by titration with a standard base solution using phenolphthalein indicator. Standard analyses were performed by Beller Laboratories, Göttingen, West Germany.

Reaction of CrO_2F_2 with $NaNO_3$. Run 1: $2NaNO_3 + CrO_2F_2 \rightarrow Na_2CrO_2F_2(NO_3)_2$. To 7.1 mmol of dried $NaNO_3$ in a ~100-ml Kel-F vessel, equipped with a Teflon-coated stirring bar and a Whitney brass valve, 6.6 mmol of CrO_2F_2 and excess (28 mmol) C_7F_{16} were added. The vessel was magnetically stirred for 3 days at room temperature. The volatile materials [C_7F_{16}, CrO_2F_2, and a trace of $CrO_2(NO_3)_2$] were removed by pumping through a trap cooled to −196°. A bright orange solid product (3.4 mmol of $Na_2CrO_2(NO_3)_2F_2$) was formed. The product did not melt but at temperatures up to 200° produced $CrO_2(NO_3)_2$, O_2, NO_2, CrO_3, and presumably NaF. The red solid, which sublimed out at 200°, melted at 198-199° (CrO_3 melts at 196°).

The powder spectrum gave the following *d* values (Å) with their respective intensities: 4.436 (s), 4.187 (m), 3.437 (s), 3.140 (s), 2.125 (m), 1.649 (m). *d* values that corresponded to $NaNO_3$ were also present. The infrared spectrum gave the following absorption bands (cm^{-1}): 1630 (w), 1350 (s), 963 (m, b), 899 (w), 875 (w), 833 (m). *Anal.* Calcd for $Na_2CrO_2F_2(NO_3)_2$: Cr, 17.8; N, 9.6; F, 13.0. Found: Cr, 14.24; N, 8.93; F, 13.1.

Run 2: $2NaNO_3 + 2CrO_2F_2 \rightarrow CrO_2(NO_3)_2 + Na_2CrO_2F_4$. To 11.8 mmol of dried $NaNO_3$, in a 100-ml polyethylene vessel, equipped with a Teflon-coated stirring bar and a Whitney brass valve, 12.0 mmol of CrO_2F_2 was added. The reactants were heated at 55-60° for 5 days. The volatile products were pumped away through a trap cooled to −196°. In addition to a deep red solid (red liquid at room temperature) a substantial amount of O_2 as determined by its molecular weight was present. The deep red solid (2.9 mmol of $CrO_2(NO_3)_2$) was shown to be essentially $CrO_2(NO_3)_2$ *via* its infrared spectrum and chemical analysis; yield 49%, based on $NaNO_3$. The infrared spectrum agreed with that previously reported.[7] Uv spectrum: $\lambda_{max}(CCl_4)$ 267 mμ (sh), 254 mμ, 400 mμ (vb), 235 mμ (vw). *Anal.* Calcd for $CrO_2(NO_3)_2$: Cr, 25.0. Found: Cr, 25.0 *via* iodometry, 24.8 *via* acidity.

To 12.9 mmol of dried $NaNO_3$, in the same reaction vessel used above, 12.9 mmol of CrO_2F_2 was added. The reaction was allowed to stand at room temperature for 12 days. The $CrO_2(NO_3)_2$ and CrO_2F_2 were separated by pumping away the CrO_2F_2 at −10 to 0°. A 5.77-mmol amount of $CrO_2(NO_3)_2$ was obtained; yield 90.5%, based on $NaNO_3$.

Preparation $Na_2CrO_2F_4$. To 23.85 mmol of dried NaF, in the same reaction vessel used in run 2, 14.75 mmol of CrO_2F_2 was added. The orange solid product (12.0 mmol of $Na_2CrO_2F_4$) was formed at 80-95° (3 days); dec pt 208°.

The powder spectrum gave the following *d* values (Å) with their respective intensities: 5.48 (m), 4.47 (vs), 3.47 (s), 3.15 (s), 2.76 (m), 2.15 (m), 2.03 (m), 2.00 (m), 1.93 (s), 1.88 (m), 1.82 (m), 1.73 (m), 1.68 (m), 1.48 (m), 1.33 (m). *Anal.* Calcd for $Na_2CrO_2F_4$: Cr, 25.3; F, 36.9. Found: Cr, 23.7; F, 34.3.

Reaction of NO_2 with CrO_2F_2. To 16.75 mmol of NO_2 in a ~100-ml silica reaction vessel, 1.13 mmol of CrO_2F_2 and 44.7 mmol of C_7F_{16} were added. The reaction proceeded for 10 days at −78°, after which the excess NO_2 (14.54 mmol) was removed. The green solid left behind corresponded to the composition $(NO_2)_{1.96}{\cdot}CrO_2F_2$. The product fumes strongly in moist air and produces NO_2 gas and a green solution on hydrolysis.

A powder spectrum showed the material to be amorphous. The infrared spectrum gave the following absorption bands (cm^{-1}): 3100 (m), 2360 (m), 1610 (s), 1510 (s), 1376 (s), 1284 (s), 961 (s), 833 (w), 768 (m). *Anal.* Calcd for $(NO_2)_2{\cdot}CrO_2F_2$: Cr, 24.3; N, 13.1; F, 17.8. Found: Cr, 24.4; N, 13.1; F, 17.0.

Registry No. $Na_2CrO_2F_2(NO_3)_2$, 36863-07-7; $CrO_2(NO_3)_2$, 16017-38-2; $Na_2CrO_2F_4$, 36788-43-9; $(NO_2)_2{\cdot}CrO_2F_2$, 12772-31-5.

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