obtained by percolating 2 ml of this purified material through a 10 × 20 mm column of activated alumina under nitrogen.

Methylcyclohexane and octane were purified in the same way. We could not purify acetic acid to the degree of purity required for these rate measurements.

Cycloalkenes.—The best commercially available cycloalkenes were purified in the same way as the hydrocarbon solvents and tightly sealed in containers under nitrogen. Immediately before use, the 0.1–0.3 ml of completely pure cycloalkene needed for an experiment was obtained by percolating 0.5 ml of carefully purified cycloalkene through a 10 × 10 mm column of alumina under nitrogen.

Samples of purified alkene which had been stored under nitrogen at −5° for more than 2 days were repurified as above before being used. Samples stored for 3 or 4 days always contained catalyst-poisoning impurities which slowed the hydrogen uptake rates and caused a divergence of the rate plots from linearity, as in Figure 2.

Hydrogenations.—In a typical experiment, 38.93 ± 0.05 mg of 0.52% platinum–alumina catalyst was added to the reaction flask. The flask was then attached to the apparatus and evacuated at 0.1 mm for 20 min while the system came to temperature equilibrium at 25.0 ± 0.1°. The system was then flushed five times with hydrogen. The addition of 0.60 ± 0.01 ml of freshly purified cyclohexane through the septum was followed by 5–10-min agitation in hydrogen at atmospheric pressure. A 0.100 ± 0.002 or 0.200 ± 0.002 ml sample of freshly purified cyclohexene was then injected, the pressure control system was quickly adjusted to 760 ± 10 mm, and agitation was started. The volume of hydrogen in the gas buret was read to the nearest 0.1 ml at 30-sec intervals. When the hydrogenation of the first sample was complete, a second sample was added using a clean hypodermic syringe and its hydrogenation was followed as above. A third sample of cyclohexene was then injected. If the rates were not constant over all three samples or if the rate plots diverged from linearity (see Figures 1 and 2), the data were discarded. An average of several values for the slopes of the linear rate plots was used to calculate the specific rates.

The rates of hydrogenation of the other cycloalkenes (Table III) were determined by substituting a sample for the middle cyclohexene sample in the experiment described above.

Temperature and Pressure Studies.—A number of hydrogen pressure dependency studies were performed using cyclohexene and cycloheptene in similar successive-sample rate measurements, but only a limited number of hydrogen dependency experiments were performed with the other cycloalkenes. Careful studies of temperature dependency were also limited to cyclohexene and cycloheptene. These studies involved three successive samples of the cycloalkene and the requirement that the observed rates be constant over all three samples.

Oxidation of Olefins by Supported Chromium Oxide

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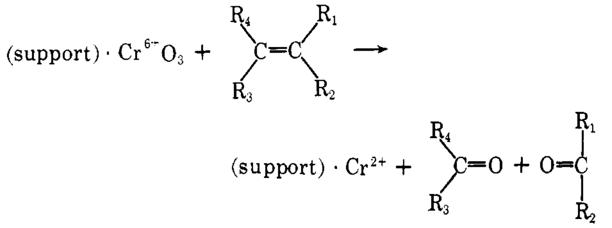
Received July 17, 1967

Olefins react with chromium trioxide supported on silica or silica–alumina to give oxidative cleavage of the double bond, with formation of the corresponding aldehydes and ketones as primary oxidation products. The chromium is reduced to the divalent state, apparently in a one-step process. A concerted mechanism is proposed to explain the observed specificity.

In the course of a general study of a variety of catalytic processes, the reaction between olefins and chromium trioxide supported on silica or silica–alumina was examined.[2] Somewhat surprisingly it was found that the supported chromium trioxide reacts rapidly and specifically with olefins to cause cleavage of the double bond and formation of the corresponding carbonyl compounds according to eq 1.



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It is well known that chromium trioxide is a powerful oxidizing agent which reacts with many organic compounds, usually giving a variety of products.[3] Therefore, the observed specificity of the supported system was sufficiently unique to warrant additional investigation of the reaction mechanism.

Experimental Section

Materials.—The silica and silica–alumina used in this work were finely divided sands of $\sim$600 m^2/g surface area, supplied by Davison Chemical Co. The supports were impregnated with an aqueous solution of chromium trioxide of appropriate concentration such that, after removal of excess impregnating solution and drying, the desired chromium level was obtained. In this work, composites containing 0.5 and 2.5% chromium were used.

Dehydration of Supported Chromium Trioxide.—The dehydration system consisted of a 2-ft section of 1-in.-diameter Vycor tubing equipped with a gas inlet, a thermocouple well, a trap at the top to collect fines, and provision to remove the product without exposure to the air. The unit was vertically mounted in an electric furnace which was equipped with a time switch to turn off the heat at the end of a preselected cycle. In most cases the composite was treated by fluidization in a stream of dry air or oxygen for 6 hr. After treatment the sand was orange or yellow.

Reaction of Ethylene with Oxides of Chromium.—The standard procedure involved heating a weighed sample of the chromium compound in an ethylene atmosphere within a glass tube of known volume equipped with a stopcock to allow sampling of the vapor space. Ethylene (40 cc at 380 mm) was heated at 200° for 16 hr over 1.0 g of finely ground chromium trioxide (Baker Analytical Grade Reagent). Periodic sampling of the vapor space and analysis by gas–liquid partition chromatography revealed an amount of carbon dioxide proportional to the period of heating, *e.g.*, after 2 hr, 36% of the olefin had been oxidized. At 250°, the oxidation of ethylene was complete within 1 hr. No evidence of ethylene polymerization was found.

In another experiment, ethylene was contacted at 150° with chromium trioxide which had been previously heated in a stream of dry air at 450° for 10 hr to afford decomposition[4] to a mixture of Cr^{3+} and Cr^{6+}. Gas chromatographic analysis revealed only ethylene present in the vapor space. At 250°, a small amount of carbon dioxide was formed indicating the presence of low concentrations of Cr^{6+}. At neither temperature was there any indication of polymerization.

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(1) Address inquiries to this author.

(2) A preliminary report of this work is covered in U. S. Patent 3,201,476 (1965), issued to the same authors.

(3) A. Byers and W. J. Hickinbottom, *J. Chem. Soc.*, 1334 (1948).

(4) M. J. Udy, "Chromium," Vol. I, Reinhold Publishing Corp., New York, N. Y., 1956.

In a third experiment ethylene was heated at 250° for 5 hr in the presence of 2.4 g of finely divided chromic oxide (Matheson Coleman and Bell, anhydrous reagent) and was recovered unchanged.

Oxidative Cleavage of Ethylene.—A 20-g sample of $CrO_3 \cdot SiO_2$ contained in a 500-ml flask immersed in an oil bath thermostatted at 125° was evacuated to a pressure below 1 mm of mercury. Ethylene gas was bled into this system at a rate sufficient to maintain a pressure of 10 mm for 1 hr. Nitrogen was then bled into the system to a pressure of 1 atm while the flask and its contents were allowed to cool to 25°. 50-ml aliquots of distilled water and cyclohexane, respectively, were added to the flask and the mixture was shaken for 10 min. A portion of the aqueous extract, when treated with chromotropic acid according to a standard procedure, gave a distinct positive test for formaldehyde.[5] The cyclohexane extract was withdrawn and dried over magnesium sulfate. The infrared spectrum of a portion of this extract exhibited no carbonyl absorption.

Determination of Chromium Valence.—A 5.0-g sample of $CrO_3 \cdot SiO_2$ catalyst containing 0.5% Cr, which had been activated at 550° for 6 hr, was placed in a 250-ml erlenmeyer flask equipped with a rubber serum stopper. It was extremely important for the purposes of this experiment that all operations be carried out with rigorous exclusion of oxygen. The reaction flask was heated to a temperature of 135° and ethylene gas was allowed to pass over the bed of catalyst for 3 min, after which the ethylene was replaced with a nitrogen atmosphere. Upon cooling below 100°, 50 ml of an aqueous electrolyte solution (1 M KCl, 0.07 M HCl), which had been purged with nitrogen for several hours to remove dissolved oxygen, was added to the flask, and the latter was vigorously agitated for 15 min. Analysis of the di- and trivalent chromium concentration was accomplished polarographically. Under these conditions, chromous ion was found to have a reversible half-wave potential, $E_{1/2} = -0.65$ V. Calibration samples were prepared by dissolving known mixtures of Cr^{2+} and Cr^{3+} in the electrolyte containing a solid phase of pure SiO_2, so as to approximate the conditions of the reaction. From the calibration standards it was possible to calculate a calibration constant $Q = 7.45$ μA/mg of Cr^{2+} contained in 6 ml of electrolyte. It should be noted that the value of Q is constant only when unknown samples are polarographed in the same electrolyte using the same dropping mercury electrode and drop time as used for calibration data. In this experiment, a 6-ml aliquot of the electrolyte extract contained 2.27 mg of Cr^{2+} and 0.40 mg of Cr^{3+}. The above experiment was repeated with ethylene contact times of 6 and 10 min, and the results are summarized in Table I. It was essential that the analyses be performed immediately after extraction, since prolonged standing at room temperature yielded continuously decreasing amounts of Cr^{2+}.

TABLE I

DETERMINATION OF CHROMIUM VALENCE[a]

Ethylene contact time, min	% Cr^{2+}	% recovery
3	85	89
6	96	87
10	86	52[b]

[a] Catalyst was 0.5% Cr on SiO_2, with 1-atm ethylene pressure, at 135°. [b] The fairly low recovery may be due to occlusion of some of the metal by polymer formation.

Olefin Oxidations.—A typical experiment involved *trans*-stilbene as the olefin and as oxidant, a chromium trioxide impregnated silica-alumina (88% SiO_2, 12% Al_2O_3) containing 2.5% Cr. Activation was accomplished by heating in a stream of air at 550° for 6 hr prior to use. A solution containing 2.02 g (11.2 mmoles) of *trans*-stilbene dissolved in 75 ml of cyclohexane was added to 23.4 g (11.2 mmoles of Cr) of catalyst under a nitrogen atmosphere at room temperature. After standing for 1 hr, the reaction mixture was triturated with 15 ml of distilled water and shaken vigorously. The cyclohexane layer was withdrawn and dried over magnesium sulfate. From the infrared absorption of the cyclohexane solution, it was apparent that the above reaction afforded conversion to benzaldehyde without formation of higher oxidation products. The per cent conversion could be estimated from the optical density at 5.84 μ, and in this experiment was 10%. Reaction of a portion of the cyclohexane extract with 2,4-dinitrophenylhydrazine reagent afforded a yellow crystalline derivative,[6] mp 234–237° (benzaldehyde-2,4-dinitrophenylhydrazone, lit. mp 237°). The 2,4-dinitrophenylhydrazone of an authentic sample of benzaldehyde was prepared and found to have mp 237–238°; a mixture melting point with the above derivative was 234–238°.

In the experiments with styrene, a portion of the aqueous extract when treated with chromotropic acid afforded a distinct positive test for formaldehyde. Control experiments using styrene and benzaldehyde individually and mixed afforded a negative test with chromotropic acid.

In one experiment, using a catalyst consisting of 2.5% Cr supported on silica, activation was accomplished by maintaining the catalyst at a pressure below 1 mm of mercury at 25° for 24 hr. Conversion of stilbene to benzaldehyde in this case was 15%.

The oxidative cleavage of tetramethylethylene was carried out by adding a solution containing 0.53 g (6.25 mmoles) of tetramethylethylene in 50 ml of cyclohexane to 13 g (6.25 mmoles of Cr) of a catalyst consisting of 2.5% Cr supported on silica. Catalyst activation was at 550° for 6 hr. After standing at room temperature for 1 hr, 50 ml of distilled water was added, and the reaction mixture was shaken vigorously. The cyclohexane layer, after drying over magnesium sulfate, exhibited an infrared spectrum in complete accord with acetone and unreacted tetramethylethylene. Because of the solubility of acetone in water the extent of reaction could not be estimated from the intensity of the carbonyl absorption.

In another experiment, 1.0 g (5.6 mmoles) of *trans*-stilbene contained in 75 ml of cyclohexane was added to 1.0 g (10 mmoles) of chromium trioxide. Vigorous agitation at room temperature afforded no obvious reaction. The mixture was then heated under reflux for 1 hr and allowed to stand at room temperature for 3 days. An infrared spectrum of a portion of the cyclohexane solution showed the presence of only stilbene; there was no evidence of any carbonyl absorption. A similar experiment using styrene also gave no oxidative cleavage of the double bond.

In one experiment, it was observed that treatment of stilbene with a $CrO_3 \cdot SiO_2 \cdot Al_2O_3$ catalyst that had not been activated, resulted in formation of benzaldehyde to the extent of 0.4%. Since the hexavalent chromium could be extracted from the catalyst upon trituration with water, it was possible that the small amount of oxidation occurred in the aqueous phase rather than on the catalyst surface. In order to test this point, 1.25 g (12.5 mmoles) of chromium trioxide dissolved in 75 ml of water was added slowly to 80 ml of a cyclohexane solution containing 2.1 g (11.6 mmoles) of *trans*-stilbene. After shaking vigorously at room temperature for 1 hr, a portion of the cyclohexane phase was withdrawn and dried over magnesium sulfate. The infrared spectrum exhibited no carbonyl absorption. It was of interest, therefore, to observe the effect of a $SiO_2 \cdot Al_2O_3$ substrate on the reaction mixture. Therefore, 24.8 g of the uncoated substrate was added to the mixture and the latter was again shaken for 1 hr. A portion of the cyclohexane phase, after drying, revealed no carbonyl absorption.

Qualitative oxidation experiments were performed using cyclohexene and vinyl cyclohexene. In both cases, the infrared spectrum of the cyclohexane extract exhibited strong carbonyl absorption, but rigorous product identification was not done.

Results

When the anhydrous $CrO_3 \cdot SiO_2 \cdot Al_2O_3$ composite was treated with ethylene it was found that 85–96% of the chromium was quickly reduced to the divalent state (Table I). Formaldehyde was the major, and perhaps sole, organic oxidation product under these conditions. In other tests, dehydrated $CrO_3 \cdot SiO_2 \cdot Al_2O_3$ or $CrO_3 \cdot SiO_2$ composites were treated with a variety of olefins and the corresponding carbonyl compounds were formed according to eq 1 and the results are summarized in Table II. In every case, the primary oxidation products were the principal

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[5] F. Feigl, "Spot Tests in Organic Analysis," Elsevier Publishing Co., New York, N. Y., 1950, p 231.

[6] R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th ed, John Wiley and Sons, Inc., New York, N. Y., 1956, p 283.

Table II

Olefin Oxidation by Supported Chromium Trioxide

Catalyst	Activation Temp, °C	Activation Time, hr	Olefin	Ratio of Cr^{6+} to olefin	Oxidation product	% yield
$CrO_3 \cdot SiO_2 \cdot Al_2O_3$[a]	550	6	Ethylene		Formaldehyde	
$CrO_3 \cdot SiO_2 \cdot Al_2O_3$[a]	550	6	Stilbene	1	Benzaldehyde	10
$CrO_3 \cdot SiO_2 \cdot Al_2O_3$[a]	550	6	Stilbene	10	Benzaldehyde	100
$CrO_3 \cdot SiO_2 \cdot Al_2O_3$[a]	550	6	Styrene	1	Benzaldehyde + formaldehyde	10
$CrO_3 \cdot SiO_2 \cdot Al_2O_3$[a]	No activation		Stilbene	1	Benzaldehyde	0.4
$CrO_3 \cdot SiO_2$[a]	550	6	Stilbene	1	Benzaldehyde	18
$CrO_3 \cdot SiO_2$[a]	25	24 (under vacuum)	Stilbene	1	Benzaldehyde	15
$CrO_3 \cdot SiO_2$[a]	550	6	Tetramethylethylene	1	Acetone	
CrO_3[b]			Styrene		No reaction	
CrO_3[b]			Stilbene		No reaction	

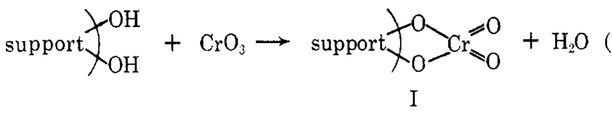
[a] 2.5% Cr. [b] Finely divided CrO_3.

products. When conversion was not complete, unreacted olefin remained in the system. In the case of stilbene at high chromium to organic ratios oxidation to benzaldehyde was complete (Table II, sample 3). Although it is well known that benzaldehyde is easily oxidized to benzoic acid, no benzoic acid was found. The combined facts that such mild reagents as olefins can cause reduction of the chromium (VI) to chromium (II) and that the olefin oxidation appears to stop at the aldehyde or ketone stage suggests a novel and specific reaction mechanism.

In control tests, unsupported chromium trioxide (bulk) did not react with ethylene at an appreciable rate at low temperature. However, at ~200° ethylene was slowly converted to carbon dioxide. Finely divided chromic oxide (Cr_2O_3) did not react with ethylene at temperatures up to 250°. Bulk chromium trioxide also failed to react with styrene and stilbene under conditions where supported chromium trioxide reacted rapidly. These tests show that the unsupported species are both less reactive and less specific than the supported species.

Discussion

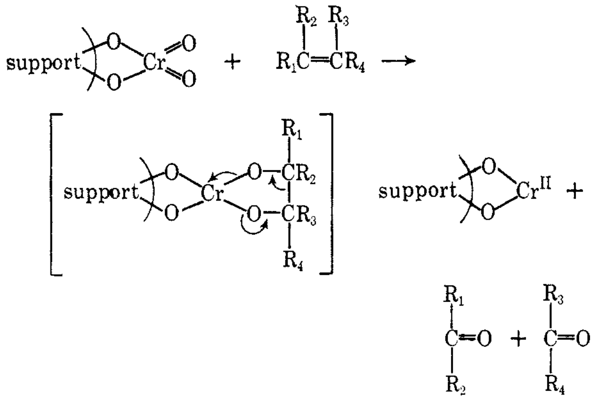
In considering possible chemical differences between supported and unsupported chromium trioxide, it should be noted that the supports, silica and silica–alumina, have hydroxyl groups at the surface[7] which may react with the chromium trioxide, in which case,



(2)

I

the activation or dehydration step is simply necessary to remove water and drive the reaction illustrated by eq 2 toward the right. It is known that surface hydroxyl groups undergo typical hydroxyl reactions[7,8] and it seems reasonable to expect similar behavior here. All the observations noted above are consistent with I being the active species in olefin oxidation. On this basis, the olefin may be envisioned as coordinating to the chromium, possibly forming an adduct, and then breaking away to give the final products (see eq 3).



(3)

This mechanism explains why the chromium is reduced to the divalent state and further explains the lack of side reactions since all the chromium oxidizing power ($Cr^{6+} \rightarrow Cr^{2+}$) is consumed in the initial step. Since the supports are excellent adsorbents, it is highly probable that the oxidation products remain bound to the support, until water is added, which would also limit side or subsequent reactions.

The supports used here are highly porous and it is reasonable that molecules of different sizes and shapes would penetrate the pores to different degrees. Whereas ethylene reduced essentially all the chromium (VI) stilbene apparently reduced only ~10% of the chromium (Table II, samples 2 and 3), although the reaction is still highly specific. This difference is probably due to failure of the large stilbene molecule to occupy fully all of the available pore space under these conditions.

Registry No.—SiO_2, 7631-86-9.

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(7) R. K. Iler, "The Colloid Chemistry of Silica and Silicates," Cornell University Press, Ithaca, N. Y., 1956.

(8) W. F. Spencer and J. E. Gieseking, *J. Phys. Chem.*, **56**, 751 (1952); C. C. Ballard, *et al.*, *ibid.*, **65**, 20 (1961).