

Oxidation of Hydroaromatic Systems. IV. The Chromic Acid Oxidation of Cycloheptatriene¹

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Abstract: In the chromic acid oxidation of cycloheptatriene, benzaldehyde in 19–25% yields is formed as the only isolable primary product; benzoic acid is obtained at higher chromic acid:cycloheptatriene ratios. The benzaldehyde isolated from the oxidation of 1,2,3,4,5,6-hexadeuteriocycloheptatriene contains $\frac{8}{7}$ of a proton per molecule evenly distributed over all available positions and must therefore be formed through a symmetrical intermediate; however, no evidence for the formation of a tropylium ion intermediate could be obtained. No significant isotope effect is observed in the oxidation of octadeuteriocycloheptatriene with chromium(VI). A mechanism for the formation of benzaldehyde consisting in a chromium(IV) oxidation of cycloheptatriene to a tropylium radical and its further oxidation by chromium(VI) directly to benzaldehyde is proposed. It is argued that the results have general validity and that the allylic oxidation products commonly formed in the oxidation of olefins with chromic acid are attributable solely to chromium(IV) and not to chromium(VI).

The ability of chromium(VI) to oxidize carbon-hydrogen bonds has been clearly demonstrated for alcohols, aldehydes, and aliphatic and alkylaromatic hydrocarbons.² The latter example is of particular importance, as it indicates that the carbon-hydrogen bond is more susceptible to oxidation than the unsaturated system of the aromatic ring.

Olefins react with chromic acid to form oxidation products derived from the oxidation of both the double bond and allylic carbon-hydrogen bonds.^{2,3} Available evidence suggests that in monoolefins chromium(VI) attacks the π -electron system.^{3c,4}

The purpose of this work was to examine whether chromium(VI) is capable of reacting with an activated σ bond in preference to a nonaromatic π bond if sufficiently favorable conditions can be provided. Cycloheptatriene (CHT) appeared particularly suitable for this purpose. Hydride abstraction from the methylene group would yield the tropylium cation, hydrogen atom abstraction the tropylium radical. The cation is well known for its quite unusual stability due to its aromatic character,^{5,7} and even the free-radical species has been shown to be stabilized to an unexpected degree.⁸ Moreover, even if hydrogen was abstracted as an atom, the transition state would be expected to assume a more polar character due to the polar and probably cationic

nature of the oxidant. We thus believe that cycloheptatriene probably provides the most favorable case for testing the ability of an oxidant to react with a carbon-hydrogen bond in preference to a nonaromatic unsaturated system.

The ability of cycloheptatriene to react both by hydride transfer from the allylic position^{9–12} and by oxidation on the unsaturated system^{13,14} has been well demonstrated. Its oxidation with chromic acid was studied as early as 1896 and found to give benzaldehyde and benzoic acid in "appreciable" yield.¹⁵ The reaction mechanism was studied by Juppe and Wolf,¹⁶ who investigated the oxidation of ¹⁴C-labeled cycloheptatriene and concluded that benzaldehyde formation involved a symmetric intermediate, assumed to be the tropylium ion.¹⁷ However, the results did not permit a decision as to whether the intermediate was formed in the rate-limiting step of the chromium(VI) oxidation, or in a subsequent reaction.

Possible mechanisms for benzaldehyde formation are represented in Scheme I. Pathway I represents the mechanism proposed by Juppe and Wolf¹⁶ combined with Doering's¹⁹ oxidation mechanism for tropylium ion. Clearly, tropylium ion could also be formed *via* other pathways, for example, from the radical (path IIa) or from double bond attack (path IIIa). The only mechanism ruled out by the results obtained by Juppe and Wolf is IIIb, namely, double bond attack followed by skeletal rearrangement.²⁰ Furthermore, an ambiguity arises from the fact that the mechanistic con-

(1) (a) Part III: F. Stoos and J. Roček, *J. Amer. Chem. Soc.*, **94**, 2719 (1972). (b) Support of this work by the U. S. Army Research Office (Durham) is gratefully acknowledged.

(2) For reviews cf. (a) K. B. Wiberg in "Oxidations in Organic Chemistry," Part A, K. B. Wiberg, Ed., Academic Press, New York, N. Y., 1965, p 69; (b) R. Stewart "Oxidation Mechanism," W. A. Benjamin, New York, N. Y., 1964, p 33; (c) J. Roček in "The Chemistry of the Carbonyl Group," S. Patai, Ed., Interscience, London, 1966, pp 467–470.

(3) (a) W. J. Hickinbottom, D. Peters, and D. G. M. Wood, *J. Chem. Soc.*, 1360 (1955); (b) F. C. Whitmore and G. W. Pedlow, *J. Amer. Chem. Soc.*, **63**, 758 (1941); (c) J. Drozd, Ph.D. Thesis, University of Illinois at Chicago Circle, 1971.

(4) (a) A. K. Aswathy and J. Roček, *J. Amer. Chem. Soc.*, **91**, 991 (1969); (b) J. Roček and J. C. Drozd, *ibid.*, **92**, 6668 (1970).

(5) The total empirical energy resonance reported⁶ for $C_7H_7^+$ is 58 kcal/mol compared with only 36 kcal/mol for benzene.

(6) G. Vincow, H. J. Dauben, Jr., F. R. Hunter, and W. B. Dolland, *J. Amer. Chem. Soc.*, **91**, 2823 (1969).

(7) E. Heilbronner and H. Bock, "Das HMO-Modell und seine Anwendungen," Verlag Chemie, Weinheim/Bergstr., Germany, 1968.

(8) The C–H bond dissociation energy in cycloheptatriene is only 73 kcal/mol.⁶ The resonance energy of the tropylium radical is reported to have a value of 31 kcal/mol, which is considerably higher than for allyl (10.2 kcal/mol), benzyl (12.5 kcal/mol), or even a triphenyl methyl (16 kcal/mol) radical.⁶

(9) P. Müller and J. Roček, *J. Amer. Chem. Soc.*, **94**, 2716 (1972).

(10) P. Müller, *Helv. Chim. Acta*, **56**, 500 (1973).

(11) D. H. Reid, M. Fraser, B. B. Molloy, H. A. S. Payne, and R. C. Sutherland, *Tetrahedron Lett.*, 530 (1961).

(12) H. J. Dauben, Jr., F. A. Gadecki, K. M. Harmon, and D. L. Pearson, *J. Amer. Chem. Soc.*, **79**, 4557 (1957).

(13) P. Müller, E. Katten, and J. Roček, *J. Amer. Chem. Soc.*, **93**, 7114 (1971).

(14) W. S. Trahanovsky, L. B. Young, and M. D. Robbins, *J. Amer. Chem. Soc.*, **91**, 7084 (1969).

(15) G. Merling, *Chem. Ber.*, **24**, 3108 (1891).

(16) G. Juppe and A. P. Wolf, *Chem. Ber.*, **94**, 2328 (1961).

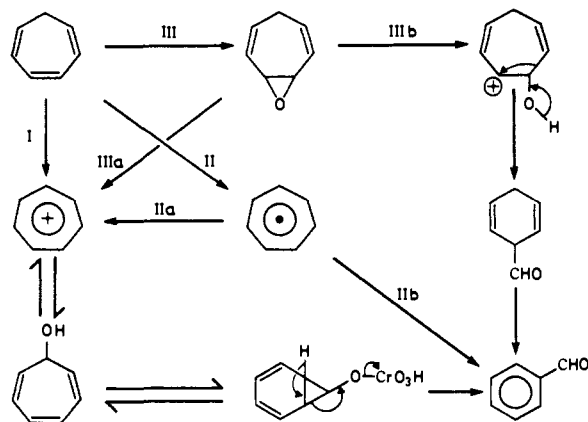
(17) The possibility of an intermediate tropylium radical was not considered.^{16,18}

(18) L. F. Fieser and M. Fieser, "Topics in Organic Chemistry," Reinhold, New York, N. Y., 1966.

(19) W. v. E. Doering and L. H. Knox, *J. Amer. Chem. Soc.*, **79**, 352 (1957).

(20) M. J. S. Dewar, C. R. Ganellin, and R. Pettit, *J. Chem. Soc.*, 55 (1958).

Scheme I



clusions were based on a yield of only 21% of the theoretically expected amount of benzoic acid. The main reaction of CHT with chromic acid could be an entirely different one. In addition to that, the stability of the specifically labeled cycloheptatriene under the reaction conditions (3 days in acetic acid) was not verified. In view of all this, the work of Juppe and Wolf was reinvestigated and extended.

Results and Discussion

Benzoic acid was isolated in 34% yield from the oxidation of cycloheptatriene in 90% acetic acid with excess chromic acid. When an excess of organic substrate was used, the yield of benzaldehyde was 19–25%, depending upon the reaction conditions. Beside small amounts of benzene and some polymeric materials, no other products could be detected, despite considerable effort. These results are in satisfactory agreement with those reported in literature, where yields varying between 21 and 34% are reported.^{14,16,21} On the other hand, oxidation of tropylium ion by chromic acid leads to benzaldehyde and benzoic acid in 90% yield.¹⁹ Accordingly, if the formation of benzaldehyde involves tropylium ion as the intermediate, this cannot be the main pathway of the reaction. The absence of any other product suggests that most of the oxidation proceeds by degradation to water-soluble carboxylic acids and carbon dioxide.

Benzaldehyde isolated from the oxidation of 1,2,3,4-, 5,6-hexadeuteriocycloheptatriene was analyzed by nmr and showed the signals corresponding to benzaldehyde. The hydrogens were equally distributed over the various positions, thereby confirming the results of Juppe and Wolf.¹⁶ Unreacted CHT-*d*₆ recovered from the reaction mixture gave a single line for the allylic protons: no protons were incorporated in the olefinic position. Mass spectral analysis of the benzaldehyde revealed the presence of penta- and hexadeuteriobenzaldehyde in a ratio of 6.0:1.0. This ratio corresponds to a mechanism in which during the first step hydrogen or hydride is lost from the allylic position, followed by a random loss of a second hydrogen or deuterium without any isotope effect.

As earlier investigators¹⁶ proposed that the symmetric intermediate is the tropylium ion, we attempted to obtain evidence which would support this assumption. Rate studies (see below) indicate that tropylium ion is less reactive toward oxidation than CHT; it

(21) L. B. Young, Ph.D. Thesis, Iowa State University, 1967.

should therefore be possible to isolate it from the oxidation products of CHT. The method used to check for the presence of the tropylium ion in the reaction mixtures was based on the separation of the ion *via* the ditropyl ether¹⁸ and isolation in the form of the sparingly soluble tropylium picrate. Tests with authentic tropylium fluoroborate added before the oxidation demonstrated that we could safely detect an amount corresponding to less than 10% of the tropylium ion yield expected on the basis of the amount of chromic acid (*ca.* 30% with respect to the yield of benzaldehyde). Nevertheless, we were unable to isolate any tropylium picrate from the oxidation of CHT.

Cycloheptatriene is known to exchange hydrogen with tropylium ions through hydride transfer reactions.²² When we oxidized hexadeuteriocycloheptatriene in the presence of unlabeled tropylium fluoroborate under conditions used in our oxidation studies, hydrogen exchange did take place and deuterated tropylium ions were formed along with undeuterated CHT. If hexadeuteriotropylium ions were formed in the course of the oxidation of hexadeuteriocycloheptatriene, they would abstract hydride ions from hexadeuteriocycloheptatriene and incorporate them into any of the seven available positions. This would lead to scrambling of hydrogen atoms over all seven carbon atoms. However, no evidence of scrambling could be detected in unreacted hexadeuteriocycloheptatriene recovered from the oxidation.

Based on the above results, we conclude that the tropylium ion is not an intermediate in the oxidation of cycloheptatriene to benzaldehyde, and that the reaction proceeds through a tropylenyl radical intermediate.²³

The kinetics of the reaction were studied in 90% acetic acid and in the presence of 2.0×10^{-3} M perchloric acid. Cycloheptatriene is stable under these conditions. Although in the course of the reaction with chromic acid CHT decomposed partially, good first-order plots for 1–2 half-lives were obtained. The oxidation of cycloheptatriene was first order in substrate over the range of 4.3×10^{-3} – 1.2×10^{-1} M. Variation of the initial chromic acid concentrations from 2.2 – 8.4×10^{-4} M produced no change on the rate constants. The rate constants of the oxidation of cycloheptatriene, perdeuteriocycloheptatriene, and some other olefins are represented in Table I. The results show that cycloheptatriene reacts about 10 to 30 times faster than monoolefins or nonconjugated dienes,²⁶ and only slightly more than twice as fast as conjugated dienes. The reactivity of the molecule thus does not reflect the stability of the tropylium ion or even of the tropylenyl radical which would be formed by hydride ion

(22) (a) G. N. Parnes, M. E. Volpin, and D. Kursanov, *Tetrahedron Lett.*, 21, 20 (1960); (b) K. Conrow, *J. Amer. Chem. Soc.*, 83, 2343 (1961).

(23) Contrary to these findings is the observation of Kursanov, *et al.*,²⁴ that tropylium ion may be isolated from the chromic acid oxidation of cycloheptatriene. Their isolation procedure consisted in the treatment of the reaction mixture with hexachloroplatinic acid, which gave tropylium hexachloroplatinate. The same product may, however, be obtained from the reaction of cycloheptatriene with hexachloroplatinic acid alone, even in the absence of chromic acid.²⁵

(24) D. N. Kursanov and M. E. Volpin, *Dokl. Chem.*, 113, 209 (1957).

(25) C. R. Kistner, J. R. Doyle, N. C. Baenziger, J. H. Hutchison, and P. Kasper, *Inorg. Chem.*, 3, 1525 (1964).

(26) The reason for the higher reactivity of 1,4-cyclohexadiene as compared with other olefins containing isolated double bonds only is not clear, and should be further investigated.

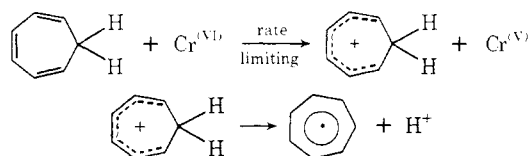
Table I. Oxidation of Olefins with Chromic Acid^a

Olefin	-10 ² k ₂ , M ⁻¹ sec ⁻¹		k _{rel}
	2.0 × 10 ⁻³ M HClO ₄	4.0 × 10 ⁻³ M HClO ₄	
Cycloheptatriene (CHT)	2.85	4.35	10.7 ^b
Perdeuteriocycloheptatriene	2.90		10.9
Cyclohexene			1.00 ^b
Tropenium fluoroborate		2.05	5.05
1-Hexene			0.29 ^b
1,4-Pentadiene			0.36 ^b
1,4-Cyclohexadiene			3.28 ^b
cis-1,3-Pentadiene			4.28 ^b
trans-1,3-Pentadiene			4.46 ^b

^a Conditions: 90% (by weight) acetic acid, 30.0°; catalyst, perchloric acid 2.0 and 4.0 × 10⁻³ M. ^b P. Ibarbia, Master's Thesis, The Catholic University of America, 1966.

or hydrogen atom abstraction. Furthermore, the reaction exhibits no isotope effect. The oxidation rates of cycloheptatriene and perdeuteriocycloheptatriene are the same ($k_H/k_D = 0.98$) within the precision of the measurements. We therefore conclude that the rate-limiting step of the oxidation is a chromium(VI) attack on the double bond.

This finding has important consequences for the understanding of chromic acid oxidations of hydrocarbons in general. It demonstrates that the reactivity of chromium(VI) toward the π -electron system of a C=C bond exceeds its reactivity toward the σ electrons of a C-H bond by many orders of magnitude, so that this difference in reactivity is not overcome even by the unique activation of the σ bond in cycloheptatriene. Consequently, there can be no doubt that in the chromic acid oxidation of olefins, chromium(VI) reacts only with the double bond and not with the allylic hydrogen. As there is ample evidence that allylic oxidation in olefins is not the result of an addition-elimination sequence, it follows that another valence state of chromium must be held responsible for allylic oxidations. We have shown that in order to explain the formation of benzaldehyde in the oxidation of cycloheptatriene one has to assume a tropanyl radical intermediate. The absence of a kinetic isotope effect rules out the formation of this radical by rate-limiting hydrogen transfer from cycloheptatriene to chromium(VI). The only mechanism by which the radical could be formed by chromium(VI) oxidation would be a rate-limiting transfer of one electron from cycloheptatriene to chromium(VI) followed by a rapid loss of a proton. We consider this

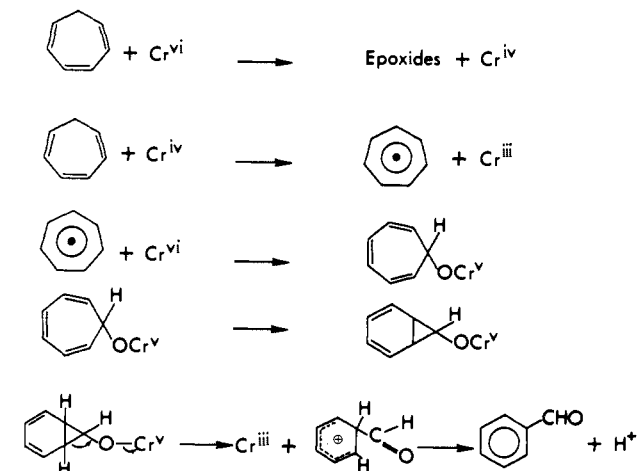


mechanism rather unlikely. It would require the formation and accumulation of an extremely strong acid, the conjugate acid of the tropanyl radical, in the presence of large amounts of a rather strong base, water. The electron transfer obviously could be very effectively assisted by a synchronous loss of a proton to the solvent, but this would result in a kinetic isotope effect.

A more plausible scheme for the formation of the radical is a direct abstraction of a hydrogen atom by

chromium(IV). This mechanism would not lead to a kinetically observable isotope effect, as the chromium(IV) oxidation would take place after the rate-limiting step, *i.e.*, after the reduction of chromium(VI). However, unlike the rate-limiting electron transfer, this mechanism should lead to an isotope effect in the product-forming step. We therefore carried out a competition experiment in which we oxidized a mixture of cycloheptatriene and 7,7-dideuteriocycloheptatriene and calculated the isotope effect from the change in the competition of the unreacted cycloheptatriene.²⁷ The method was tested by determining the isotope effect for the reaction of cycloheptatriene with triphenylmethyl perchlorate in acetonitrile.¹² A value of 3.0 was obtained, in reasonable agreement with Dauben's result, 5.0, for the isotope effect of the reaction between cycloheptatriene and the dianisylmethyl cation.²⁸ For chromic acid the isotope effect was 1.61 ± 0.02 . This value corresponds to the overall isotope effect. The isotope effect for chromium(IV) alone may be approximately evaluated if it is assumed that an equal number of molecules of cycloheptatriene reacts with chromium(IV) (with isotope effect) as with chromium(VI) (no isotope effect; *cf.* Scheme II). This assumption leads

Scheme II



to an estimate of $k_H/k_D = 2.4$ for the chromium(IV) oxidation of cycloheptatriene, a value which is only slightly higher than isotope effects observed in the chromium(IV) oxidation of isopropyl alcohol ($k_H/k_D = 1.9$),²⁹ propionaldehyde ($k_H/k_D = 1.7$),³⁰ and pivaldehyde ($k_H/k_D = 2.1$).³⁰

The observed isotope effect thus offers strong support for the assumption that the tropanyl radical is formed by direct hydrogen atom transfer from cycloheptatriene to the chromium(IV).³¹ This result also supports our suggestion that the chromium(IV) intermediate is responsible for the formation of allylic oxidation products observed in the chromic acid oxidation of olefins.

(27) G. A. Russell and R. C. Williamson, *J. Amer. Chem. Soc.*, **86**, 2357 (1964).

(28) H. J. Dauben, Jr., and L. M. Donough, quoted by K. E. Wiberg and E. L. Mottell, *Tetrahedron*, **19**, 2009 (1963).

(29) M. Rahman and J. Roček, *J. Amer. Chem. Soc.*, **93**, 5455, 5462 (1971).

(30) J. Roček and C. S. Ng, *J. Amer. Chem. Soc.*, **96**, 1522 (1974).

(31) It should be noted that chromium(IV) reacts with cycloheptatriene differently than a previously investigated one-electron oxidant, cerium(IV), for which the rate-limiting step was addition to a double bond.¹³

The main reactions taking place during the chromic acid oxidation of cycloheptatriene can be summarized in Scheme II. The first step is a rate-limiting reaction of chromium(VI) with cycloheptatriene leading to a product of a double bond oxidation, probably an epoxide, which undergoes further oxidation to products which we were unable to isolate. Chromium(IV) formed in the rate-limiting step reacts with cycloheptatriene to form a tropenyl radical, which is oxidized further to benzaldehyde. It should be noted that a one-electron oxidation of the radical would lead to the tropenium ion or to 7-hydroxy-1,3,5-cycloheptatriene, which should be in equilibrium with the ion. Our failure to detect any evidence of tropenium ion formation thus suggests that the chromium(V) intermediate most likely formed from the radical and chromic acid undergoes very rapid oxidative decomposition before it can hydrolyze. The absence of any observable isotope effect in the formation of benzaldehyde from hexadeuteriocycloheptatriene (*vide supra*) indicates that the breaking of the carbon-hydrogen bond in the oxidation of the tropenyl radical to benzaldehyde occurs at a stage where there is no option between hydrogen and deuterium loss. A possible pathway involving the formation of a benzenium ion intermediate is suggested in Scheme II.

The norcaradiene intermediate is a chromium(V) ester of a substituted cyclopropanol. Its very rapid oxidative decomposition is in full agreement with the recently observed extremely high reactivity of cyclopropanols³² toward chromic acid oxidation by a mechanism involving the cleavage of the cyclopropanol ring.

Experimental Section

Materials. Acetic acid (99.5%, Fisher Chemical Co.) was used throughout the work. CHT (Aldrich Chemical Co.) was purified by distillation. For kinetic measurements it was further purified by glpc. The preparation of perdeuteriocycloheptatriene has been described.³³ 7,7-Dideuterio- and 1,2,3,4,5,6-hexadeuteriocycloheptatriene were obtained by the decomposition of deuterated and undeuterated diazomethane in the presence of benzene or hexadeuteriobenzene, respectively, and cuprous chloride.^{33,34}

Instrumentation. Nmr spectra were obtained on a Varian A 60-A instrument, ir spectra on a Beckman IR-10, and low-voltage mass spectra for the isotope effect at *ca.* 11 eV on an Atlas CH 4 instrument. For analytical glpc a 10-ft Carbowax column was used in an F&M Analytical gas chromatograph, Model 5560. Preparative gas chromatography was done on a F&M Prepmaster Jr. 776 with a Carbowax column.

Yields of Benzaldehyde and Benzoic Acid. A. Excess CHT. CHT (10.0 g) was reacted with 1.45 g (14.5 mmol) of chromium trioxide in 70 ml of 90% acetic acid ($[\text{HClO}_4] = 2.0 \times 10^{-3} M$) for 18 hr. After addition of 100 mg of sodium bicarbonate the mixture was distilled on a vacuum line. The liquid was analyzed by glpc; it contained benzaldehyde in a 19.5% yield, based on chromium trioxide. Beside a small amount of benzene no other volatile products were found. The solid residue gave a precipitate with dinitrophenylhydrazine, containing traces of benzaldehyde (by tlc) and unseparable products, presumably polymers.

B. Sodium Acetate and Excess CHT. Potassium dichromate (160.9 mg, 0.347 mmol) was suspended in 10 ml of 90% acetic acid. Sodium acetate (1.00 g) and 1.00 g of CHT in 10 ml of acetic acid (90%) were added and the solution was stirred for 48 hr. Work-up procedure as mentioned above. Yield 24.5%, calculated on potassium dichromate.

C. Excess Chromic Acid. Chromium trioxide (1.00 g) was dissolved in 20 ml of 90% acetic acid, and CHT (151.7 mg) in 10 ml of acetic acid (90%) was added dropwise. After 17 hr, 50 ml of water was added and the solution was extracted with ether. The ether was evaporated and the residue purified by sublimation. Yield 68.4 mg (0.56 mmol) of benzoic acid (34%) identified by ir and mixture melting point (complete conversion of a 1% toluene impurity to benzoic acid is assumed).

Oxidation of Hexadeuteriocycloheptatriene. CHT-*d*₆ (414 mg, 4.22 mmol) was dissolved in 10 ml of 90% (by volume) acetic acid, at a perchloric acid concentration of $2.0 \times 10^{-3} M$. Chromium trioxide, 565 mg (5.65 mmol), was added in 10 ml of the same solvent during 15 min. The mixture was then stirred for 3 hr. After dilution with 50 ml of water, it was extracted with five 10-ml portions of carbon tetrachloride. The combined extracts were washed three times with sodium hydroxide solution and twice with water, dried with sodium sulfate, and concentrated by distillation. The residue was purified by bulb-to-bulb distillation on a vacuum line. Benzaldehyde and CHT were found to be present, by glpc, without major impurities. Separation was obtained by preparative glpc. Only a single proton peak was visible in the nmr spectrum, corresponding to the aliphatic group of cycloheptatriene. The benzaldehyde gave signals for the four types of protons present with the normal intensities. From low-voltage mass spectroscopy (Atlas CH-4) the benzaldehyde was found to give two parent peaks, at *m/e* 111 and 112, with the intensities 5.96 and 1.0.

Attempts for Isolation of Tropenium Ion. CHT, *ca.* 10 g, was dissolved in 50 ml of 90% acetic acid at a perchloric acid concentration of 2.0 or $4.0 \times 10^{-3} M$ and tropenium fluoroborate (0.79–2.79 mmol) was added. Chromium trioxide, 720–820 mg, in 90% acetic acid was added dropwise under magnetic stirring, which was continued for 1 hr after the addition. The solution was diluted with 500 ml of water and extracted with three 100-ml portions of ether. The aqueous layer was neutralized with solid sodium bicarbonate until evolution of carbon dioxide ceased; 100 ml of 2 *N* sodium hydroxide was added and the solution extracted four times with 60 ml of ether. After drying of the ether with sodium sulfate, 100 ml of saturated picric acid solution in ether was added. The tropenium picrate was separated and recrystallized from water. Yield of recovery was *ca.* 55%; identification by ir and nmr with an authentic sample. At lower concentrations (below 8% of the expected amount) and in the absence of added tropenium fluoroborate no picrate could be obtained.

Oxidation of Hexadeuteriocycloheptatriene in the Presence of Tropenium Ion. CHT-*d*₆ (773 mg, 7.9 mmol) was added to 1.40 g of tropenium fluoroborate (8.7 mmol) in 50 ml of 90% acetic acid ($[\text{HClO}_4] = 2.0 \times 10^{-3} M$) and 1.050 g of chromium trioxide (10.5 mmol) in 25 ml of solvent was added as quickly as possible. After 30 min the solution was diluted with 200 ml of water and extracted with six 50-ml portions of ether (extract A). The aqueous layer was neutralized with solid sodium bicarbonate and sodium hydroxide solution and extracted with ether (extract B).

Extract A contained unreacted CHT. The ether was displaced by carbon tetrachloride and the solution analyzed by nmr. The composition was *ca.* 54% CHT-*d*₆ and 46% undeuterated CHT. Extract B was dried overnight with sodium sulfate and the ditropyl ether, formed from tropenium ion, was reduced with lithium aluminum hydride. Excess lithium aluminum hydride was decomposed with dilute acetic acid. The ether was washed with sodium hydroxide and water and dried, and the solution concentrated. CHT (108 mg) was purified by preparative glpc. Low-voltage mass spectroscopy on a Hitachi-Perkin-Elmer instrument Model 270 gave a composition of 54.5% undeuterated CHT, 43.9% CHT-*d*₆, 1.4% CHT-*d*₇, and 0.2% CHT-*d*₁.

Kinetic Measurements. Chromic acid solutions were prepared by dissolving chromium trioxide in 90% w/w acetic acid; 0.6 ml of perchloric acid $10^{-2} M$ in 90% acetic acid was added to 0.4 ml of chromic acid solution and 2.0 ml of 90% acetic acid. The solution, *ca.* $5 \times 10^{-4} M$ in chromic acid and 2.0×10^{-3} in perchloric acid, was thermostated for 15 min in the cell compartment of a Zeiss PMQ II spectrophotometer at 30.0°. CHT, *ca.* 10 μ l, was then injected with a syringe, the cell was shaken, and readings at 350 nm were taken at suitable time intervals. The readings were corrected for the absorbance of CHT at *t*₀. No infinity readings were obtained, because of decomposition of the CHT. First-order plots gave straight lines almost to 2 half-lives (see Figure 1). The second-order rate constant of undeuterated CHT was corrected for a toluene impurity of 6.6%. The results of the runs for the determination of the isotope effect are given in Table II.

Determination of the Isotope Effect by Competition Experiment.

(32) J. Roček, A. M. Martinez, and G. E. Cushmac, *J. Amer. Chem. Soc.*, **95**, 5425 (1973).

(33) P. Müller and J. Roček, *J. Org. Chem.*, **33**, 3001 (1968).

(34) E. Müller and H. Fricke, *Justus Liebig's Ann. Chem.*, **661**, 38 (1963).

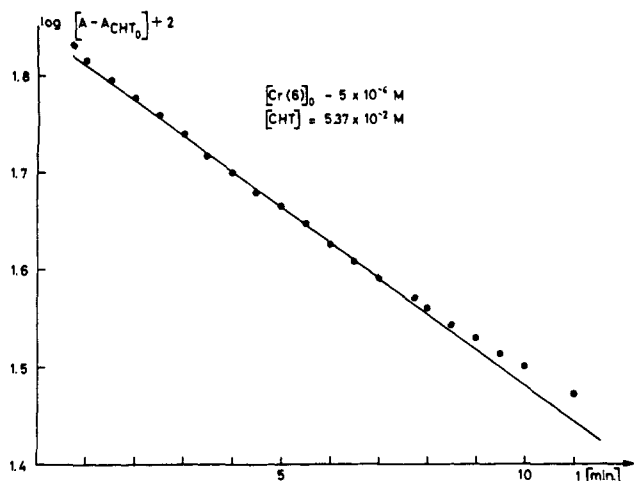


Figure 1. Sample run of the oxidation of CHT with chromic acid.

Table II. Determination of the Isotope Effect of Cycloheptatriene with Chromic Acid

Substrate	Concn, $\times 10^{-2} M$	$10^2 k_2, M^{-1} \text{sec}^{-1}$	Av	k_H/k_D
CHT	5.37	2.82	2.85	0.98
	5.58	2.84		
	5.81	2.92		
CHT- d_3	4.48	3.04	2.90	
	4.33	2.73		
	6.20	2.97		

A mixture containing CHT and CHT- d_2 in ca. 30 ml of 90% acetic acid (757 mg) was oxidized for 3 hr with 772 mg of potassium dichromate at room temperature. The volatile part of the solution was distilled on a vacuum line. A known amount of ethanol was added as standard, and the amount of recovered CHT (515 mg) was determined by glpc. The solution was then diluted with water. CHT was extracted with ether and purified by preparative glpc. The isotopic composition of the CHT before and after the oxidation

was determined by low-voltage mass spectrometry. The initial mixture had peaks at m/e 92 (46.3%), 93 (9.1%), and 94 (44.6%), the values representing the average of nine measurements with a standard deviation of ± 0.2 . After correction for ^{13}C the composition is 48.3, 5.7, and 46.0%. The peak at m/e 91 had an intensity below 2% and could not be determined precisely owing to the small signal/noise ratio. No correction was therefore applied for fragmentation of the CHT. The composition of the recovered CHT (two measurements) was 41.3, 10.2, and 48.5%. (A third determination with 41.2, 9.3, and 49.5% was not included in the calculation.) After correction for ^{13}C the composition was 42.8, 7.3, and 49.8%. For the computation of the CHT a correction for a toluene impurity was applied (4% in the CHT- d_2 before and 5% after the reaction). Accordingly the initial CHT mixture contained 362 mg of CHT, 339 mg of CHT- d_2 , and 41 mg of CHT- d . The recovered CHT was composed of 218 mg of CHT, 248.5 mg of CHT- d_2 , and 36 mg of CHT- d . The isotope effect was calculated with

$$k_H/k_D = \frac{\log \{ \text{CHT}_E / \text{CHT}_0 \}}{\log \{ d_2\text{-CHT}_E / d_2\text{-CHT}_0 \}} = 1.61 \pm 0.2 \quad (1)$$

The indices E and 0 correspond to the concentrations at the end and at the beginning of the reaction. The applicability of eq 1 requires that the reaction rate of CHT- d (k_{HD}) = $1/2 k_{HH} + 1/2 k_{DD}$. The experimental error is estimated from the error in the mass spectra (5.5%) and from the determination of the CHT (2%). To this is added a systematic error of 5% for systematic errors, such as baseline error and potential loss of CHT during the vacuum line distillation.

Isotope Effect with Triphenylmethyl Perchlorate. A mixture of CHT (122 mg), CHT- d_2 (112 mg), and CHT- d (16 mg) in 5 ml of dry acetonitrile was reacted with 177 mg of triphenylmethyl perchlorate.³⁵ After 5 min the flask was frozen with liquid nitrogen and the volatile components were removed by bulb-to-bulb distillation. The residue was extracted with ether to yield, after evaporation and sublimation, 113.6 mg (0.46 mmol) of triphenylmethane, mp 92°. The volatile fraction consisted of 93.5 mg of unreacted CHT and 107.5 mg of CHT- d_2 as calculated from the isotopic composition of the isolated triphenylmethane (24.9% monodeuterio compound). Calculation as above gave $k_H/k_D = 2.95 \pm 0.2$.

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Chromium(IV) Oxidation of Aromatic Aldehydes

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Abstract: The previously introduced method for the study of chromium(IV) oxidations in which chromium(IV) is generated *in situ* in the course of the reduction of chromium(VI) by vanadium(IV) was adapted for use with water-insoluble substrates. The chromium(IV) oxidation of substituted aromatic aldehydes gave a value of $\rho = +0.97$. A mechanism consisting of a rate-limiting decomposition of a chromium(IV) complex of the aldehyde hydrate is proposed. The results permitted the recalculation of the ρ value for the chromium(V) oxidation of aromatic aldehydes using results obtained earlier by Wiberg and Richardson; a value of $\rho = +0.30$ was obtained.

The chromium(VI) oxidation of vanadium(IV) in the aqueous system has been extensively studied by Espenson, who showed that the reaction followed Scheme I.¹ We have previously employed this system successfully in the study of the chromium(IV) oxidation of alcohols,^{2,3} aliphatic aldehydes,⁴ and oxalic acid.⁵

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However, our studies thus far have been confined to the aqueous system in which a great many organic compounds have only limited solubility.

The purpose of this work was to develop a method which would permit the study of chromium(IV) oxidations of water-insoluble substrates. We found that

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